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ELECTRON OXIDATION OF AROMATIC MOLECULES
AND RELATED DELOCALIZED-ELECTRON SOLIDS

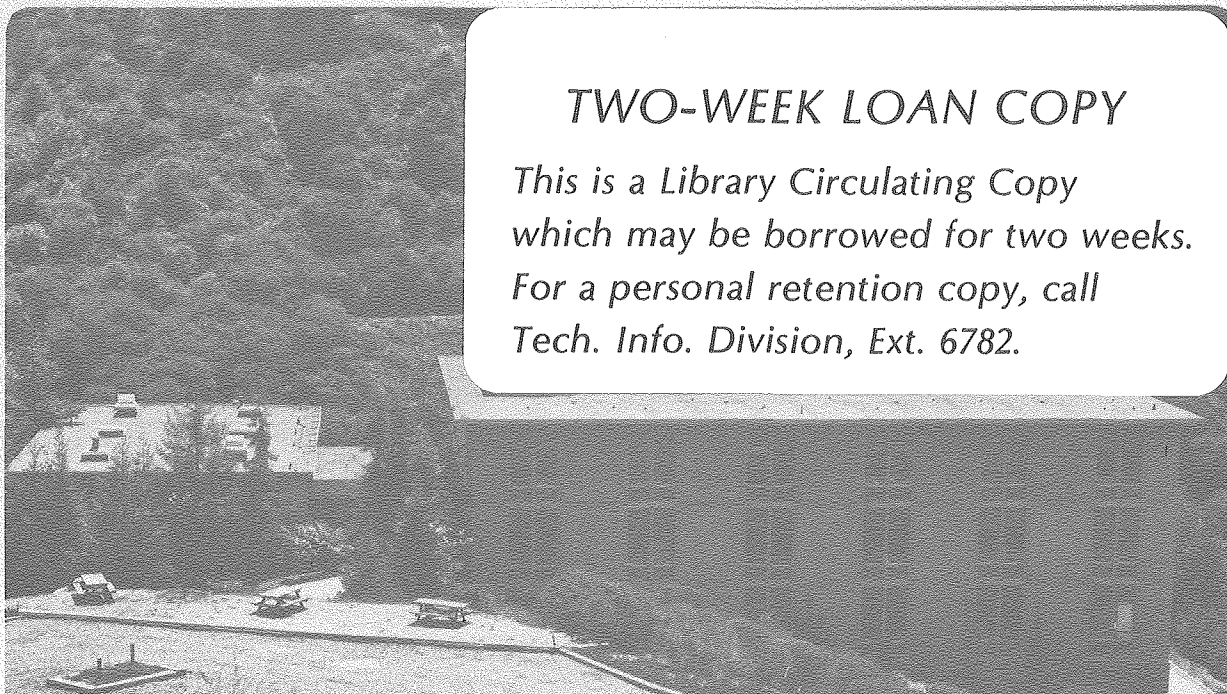
Francis Louis Tanzella
(Ph.D. thesis)

January 1980

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Electron Oxidation of Aromatic Molecules and
Related Delocalized-Electron Solids

By

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RELATED DELOCALIZED-ELECTRON SOLIDS

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ELECTRON OXIDATION OF AROMATIC MOLECULES AND
RELATED DELOCALIZED-ELECTRON SOLIDS

Francis Louis Tanzella

ABSTRACT

Efficient syntheses for the previously synthesized salts $C_6F_6AsF_6$ and $C_{10}F_8AsF_6$ have been developed. The salts $C_5F_5NAsF_6$ and $CF_3C_6F_5AsF_6$ have been prepared from the interaction of O_2AsF_6 with pentafluoropyridine and octafluorotoluene, respectively. The thermal decomposition of $C_6F_6AsF_6$, $C_5F_5NAsF_6$ and $CF_3C_6F_5AsF_6$ yields an equimolar mixture of the parent fluorocarbon and an isomer-specific cyclohexadiene. A mechanism for this decomposition involving F^- transfer from anion to cation is discussed. Hydrolysis of $C_{10}F_8AsF_6$ yields an equimolar mixture of $C_{10}F_8$ and an isomer-specific quinone $C_{10}F_6O_2$. A mechanism involving OH^- attack on the cation, similar to the F^- attack above, is presented.

Benzene reacts quantitatively with AsF_5 to give $(C_6H_5)_2AsF_2^+AsF_6^-$, the first reported aryl or alkyl fluoroarsonium(V) salt. This reacts quantitatively with CsF to give $(C_6H_5)_2AsF_3$ and $CsAsF_6$. Interaction of $(C_6H_5)_2AsF_3$ with AsF_5 reconstitutes the fluoroarsonium salt. Variable temperature ^{19}F NMR studies show ϕ_2AsF_3 to be a rigid trigonal bipyramid, with the phenyl groups in equatorial positions, to $71^\circ C$. Interaction of benzene with O_2AsF_6 or $C_6F_6AsF_6$ yields a mixture of $(C_6H_5)_2AsF_2^+AsF_6^-$ and a poly(p-phenylene) salt $\{C_6H_4\}_xAsF_6$ ($1.8 < x < 4.4$).

A mechanism involving initial electron oxidation of benzene to give the radical cation intermediate $\text{C}_6\text{H}_6^+\text{AsF}_6^-$ is proposed. The moderate electrical conductivity of the polyphenylene salt indicates that it is a delocalized-electron solid.

Preliminary results on the electron oxidation of naphthalene, anthracene and phenanthrene suggest the formation of AsF_6^- salts of these aromatics.

Interaction of coronene with O_2AsF_6 or $\text{C}_6\text{F}_6\text{AsF}_6$ yields a dark-green colored powder which is shown to be a mixture of products. The moderate electrical conductivity of the mixture indicates that at least one component in the mixture is a delocalized-electron solid. Lack of well-crystallized products has been a major difficulty in these studies.

Neil Bartlett

I. INTRODUCTION

This work is a study of the products formed from the electron oxidation of aromatic molecules. Earlier studies on the oxidation of perfluoroaromatics have been reexamined and extended to include pentafluoropyridine and octafluorotoluene. The interaction of benzene with strong oxidizing agents has also been undertaken. The solution of this latter complicated oxidation led to investigation of the interaction of benzene with AsF_5 . Recognition that cations derived from naphthalene, anthracene and coronene would be much larger than the counter ion (AsF_6^-) stimulated interest in such salts. The anticipated close-packing and consequent overlap of the aromatic species orbitals, was perceived as providing for the possibility of extensive electron delocalization. Such salts were therefore prepared in the hope that they would prove to be semimetallic or metallic.

Apparatus common to much of the experimental work and general experimental techniques are collected in Chapter II.

Chapter III is devoted to efforts to find efficient syntheses for the previously prepared $\text{C}_6\text{F}_6^+\text{AsF}_6^-$, $\text{C}_{10}\text{F}_8^+\text{AsF}_6^-$, $\text{C}_5\text{F}_5\text{N}^+\text{AsF}_6^-$,^{2,3} and $\text{CF}_3\text{C}_6\text{F}_5^+\text{AsF}_6^-$ salts. Magnetic and structural studies were also undertaken wherever possible, to characterize the cations. The room-temperature thermal decomposition products of these salts have been investigated and have indicated that F^- transfer from the anion

to the cation occurs and gives an equimolar mixture of the parent fluorocarbon and a cyclohexadiene. The stereoselectivity of these reactions are demonstrated as well as the stereospecific hydrolysis of $C_{10}F_8^+AsF_6^-$. Mechanisms are proposed.

Chapter IV deals with the preparation of $(C_6H_5)_2AsF_2^+AsF_6^{3-}$. This salt is one of the products formed from the electron oxidation of benzene. It is quantitatively formed from the interaction of AsF_5 with benzene in a suitable solvent. The characterization of this salt is described and in the process a novel method is described for the efficient and clean synthesis of $(C_6H_5)_2AsF_3$.

Chapter V describes the reaction of C_6H_6 with O_2AsF_6 and $C_6F_6AsF_6$. Two compounds are produced, the previously discussed $(C_6H_5)_2AsF_2^+AsF_6^-$ and an AsF_6^- salt of poly(p-phenylene).⁵ The analysis and physical and chemical characterization of the polyphenylene salt are described.

Attempts to synthesize metallic or semiconducting salts from the larger ring hydrocarbons such as naphthalene, anthracene and coronene, using the oxidizing agents O_2AsF_6 , $C_6F_6AsF_6$ and AsF_5 are described in Chapter VI. The physical and chemical properties of the radical cation salts formed are described. Factors which determined the attainable cation charges are also considered.

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II. GENERAL APPARATUS AND PROCEDURES

A. Apparatus

1. General

Since most of the materials handled in this work hydrolyze quickly upon exposure to moist air, meticulous care was taken to maintain dry vessels and handling apparatus. The powerful oxidizers and other reagents used in this work required unconventional container materials and special fabrications.

A Vacuum Atmospheres Corporation Dri-Lab (North Hollywood, California) was used for the manipulation of all solids and less volatile liquids in a dry nitrogen atmosphere. Water and oxygen were scrubbed from the system using a molecular sieve drying tower and a catalytic oxygen scavenger which were regenerated on a regular schedule. Light bulb filaments open to the inert atmosphere were kept glowing to detect water or oxygen.

Volatile compounds were transferred in a vacuum line constructed from Stainless Steel Whitey LKS4-SS valves with appropriate stainless steel Swagelok fittings and tubing. Vacuum was provided by a large capacity mechanical pump connected to a glass center-trap maintained at -196° . Line access to the vacuum pumps was either direct or by way of a soda-lime tower to scrub fluorine or other oxidizers. High-vacuum capability was available from a large glass manifold connected to a two-inch Consolidated Vacuum Corporation silicone-oil diffusion pump with a large mechanical forepump. A cylindrical monel bomb equipped with an Autoclave Engineering 30Vm 6071 monel valve was used for reac-

tions at high temperature and pressure.

Low pressures (<1mm) were measured using a NRC (Varian Corporation) thermocouple gauge and controller. Pressures up to 1500mm were determined with a monel Helicoid gauge specifically constructed for fluorine and oxygen service and supplied by ACCO Helicoid Gage (Bridge Port, Connecticut).

2. Teflon FEP and KEL-F Reaction Vessels

Teflon reaction vessels were constructed from 1/2" OD Teflon FEP Tubing (Plastic Sales, Oakland, California) which was sealed at an appropriate length (8") by crimping with flat-nosed pliers which had been heated over a bunsen burner. Each tube was connected to a Whitey 1KS4-SS valve via a 1/2" to 1/4" stainless steel Swagelock reducing union and 1/4" stainless steel tubing. Teflon TFE ferrules were used for all swaged fittings.

Kel-F vessels were made by connection of a molded Kel-F tube (obtained from Argonne National Laboratories) to a Kel-F fitting as shown in Figure II-1. The fitting was threaded to accept a Kel-F valve with a 1/4" Kel-F tube attached by Teflon compression fittings. When a solid aromatic was to be reacted with $O_2^+AsF_6^-$ a disc of Teflon TFE filter paper (Cole Palmer Laboratories) was used to separate the two reactants.

3. Teflon Filtration Apparatus

The apparatus shown in Figure II-2 was used for filtrations with anhydrous HF as the solvent. A disc of

TFE filter paper (1" diameter) was placed over the end of a FEP tube (0.5" OD) which was forced into a like piece of tubing which had been stretched by a hot glass spindle. The junction was fused using a hot air gun so as to provide a leak tight and firm seal for the FEP tubes and filter disc. The junction was helium leak-tested on cooling.

4. Apparatus for Measuring Resistivity

Crude resistivity measurements were made by pressing a powdered sample into a Kel-F tube (1mm i.d.) with two 1mm copper rods. The direct resistance so measured was used to calculate the resistivity.

B. Reagents

1. Gases and Volatile Liquids

F₂, SO₂ and HF were supplied by Matheson Gas Products (East Rutherford, New Jersey). F₂ was used as received. SO₂ was condensed onto and stored over phosphorous pentoxide. HF was treated with F₂ (2 atm pressure) before being condensed onto and stored over K₂NiF₆. SF₄ was used as supplied by Air Products (Allentown, Pennsylvania). AsF₅ and SO₂ClF were supplied by Ozark Mahoning Pennwalt (Tulsa, Oklahoma). AsF₅ was purified in the cylinder by removing non-condensable gases via several freeze-pump-thaw cycles from -196°. The SO₂ClF was distilled immediately before each reaction. To remove oxidizable impurities the solvent was condensed onto O₂AsF₆ and allowed to react at -45°. All volatiles were removed at -78°. The vessel was never

warmed above -45° when it was used as a source of SO_2ClF .

Spectroscopic quality C_6H_6 , $\text{CH}_3\text{C}_6\text{H}_5$ and $(\text{CH}_3)_2\text{SO}$ were supplied by Matheson, Coleman and Bell (Norwood, Ohio).

C_6H_6 was condensed onto and stored over lump sodium.

$\text{CH}_3\text{C}_6\text{H}_5$ and $(\text{CH}_3)_2\text{SO}$ were dried and stored over molecular sieves.

C_6F_6 , C_5NF_5 and $\text{CF}_3\text{C}_6\text{F}_5$ were supplied by P. C. R. Inc. (Gainesville, Florida). C_6F_6 was condensed onto and stored over phosphorous pentoxide. C_5NF_5 and $\text{CF}_3\text{C}_6\text{F}_5$ were degassed via several freeze-pump-thaw cycles.

2. Solids

Naphthalene (C_{10}H_8), anthracene ($\text{C}_{14}\text{H}_{10}$) and coronene ($\text{C}_{24}\text{H}_{12}$) were supplied by Aldrich Chemical (Milwaukee, Wisconsin). C_{10}H_8 was recrystallized from hot methanol. $\text{C}_{14}\text{H}_{10}$ was recrystallized from hot ethanol. $\text{C}_{24}\text{H}_{12}$ was recrystallized from hot benzene. C_{10}F_8 was used as received from P. R. C. Inc. $(\text{C}_6\text{H}_5)_2\text{AsOOH}$, supplied by Research Organic/Inorganic (Sun Valley, California) was recrystallized from CCl_4 . CsF was used as received from Alfa Ventron (Beverly, Massachusetts).

O_2AsF_6 was prepared as described previously with the following modification: the reaction bulb (5 liters) and adjacent mercury lamp were wrapped with a large piece of aluminum foil to increase the efficiency of the light source. The reaction was 85% complete overnight.

C. Instrumentation

1. Infrared Spectroscopy

Infrared spectra were obtained in the $4000\text{--}200\text{ cm}^{-1}$ range on a Perkin Elmer Model 597 spectrometer. Spectra of gases were obtained in a 10 cm path length Monel gas cell with AgCl windows. These windows were cut from a one millimeter sheet supplied by Harshaw Chemical Co. (Cleveland, Ohio). Spectra of solids were run on either a fine dusting of powder, a mineral oil mull or a pressed potassium bromide pellet, each held between two silver chloride windows.

2. Raman Spectroscopy

Raman spectra were recorded using a Jobin-Yvon Ramanor HG2S double monochromator. Two lasers, a Spectra Physics Model 165 Krypton ion and a Coherent Radiation Model CR-2 Argon ion, were used as sources for the three wavelengths for excitation (blue 488.0 nm, green 514.5 nm, and red 647.1 nm).

Samples were loaded into thin-walled quartz capillaries (Charles Supper Company, Natick, Massachusetts) in the Dri-Lab. They were sealed temporarily with a plug of Kell-F grease and the tube was drawn down in a small flame outside the box. To counteract fluorescence and thermal decomposition, some samples were cooled by flowing dry N_2 which was itself cooled by passage through a 3/8" diameter copper coil immersed in liquid N_2 (-196°).

3. X-Ray Powder Photography

X-Ray powder photographs were obtained using a General Electric Precision Powder Camera of 45 cm circum-

ference (Straumanis Loading) with Ni-filtered Cu- k_{α} radiation. Finely powdered samples were loaded into 0.3-0.5mm thin-walled quartz capillaries in an identical manner to that described under Raman Spectroscopy. X-Ray films were measured on a Norelco film measuring device.

4. Magnetic Susceptibility

Magnetic susceptibility measurements were made using a Princeton Applied Research Vibrating Sample Magnetometer in the temperature range 4-100° K. Solid samples were loaded into specially fabricated Kel-F tubes. A tight-fitting plug was pressed down firmly onto the sample to ensure good packing.

5. Analysis

(a) Routine C, H, As and F

Routine C and H analyses were performed by the Micro-analytical Laboratory in the College of Chemistry. Routine As and F analyses were performed by Galbraith Laboratories (Knoxville, Tennessee).

(b) Fluorine by Potassium Fusion

For materials containing fluorine bound to carbon, which cannot be determined accurately via routine fluorine analysis, a potassium fusion technique was used. A weighed amount of the sample along with an excess of lump potassium were placed in a drilled out 3/8" monel rod with a tight-fitting monel Swagelock cap. The tube was heated upright at 900° for 4 hours, and the excess potassium destroyed with dry ethanol. The product was digested in hot

water and the F^- precipitated and weighed as $PbClF$.² The $PbClF$ determination was performed in the College of Chemistry Microanalytical Laboratory.

6. Mass Spectroscopy

Mass spectra were obtained using an AEI MS12 Spectrometer. Samples (approximately $50\mu g$) were sealed in a quartz capillary in an identical manner to that described under Raman Spectroscopy. The samples were placed in an evacuated vessel open to the ionization chamber. The capillary was then broken mechanically in this vessel and the volatiles were admitted to the ionization chamber. Less-volatile samples were introduced in the same manner and the sample chamber was heated.

7. NMR and ESR Spectroscopy

Routine 1H and ^{19}F NMR spectra were recorded on a Varian EM-390 90MHz spectrometer equipped for proton and fluorine capability. Some ^{19}F NMR spectra were recorded on a Varian NV-14 equipped for fluorine use operating at 56.4 MHz. Air sensitive samples were dissolved and loaded in the glove box.

When extremely volatile solvents or standards were used, the NMR tube was connected to a Whitey valve with Swagelok connections using teflon ferrules. The liquids were vacuum distilled into the tube and the tube drawn down with a small flame.

ESR spectra were recorded on samples in quartz tubes on a Varian Model E-3 Spectrometer. Samples were loaded

in a similar manner to that described above.

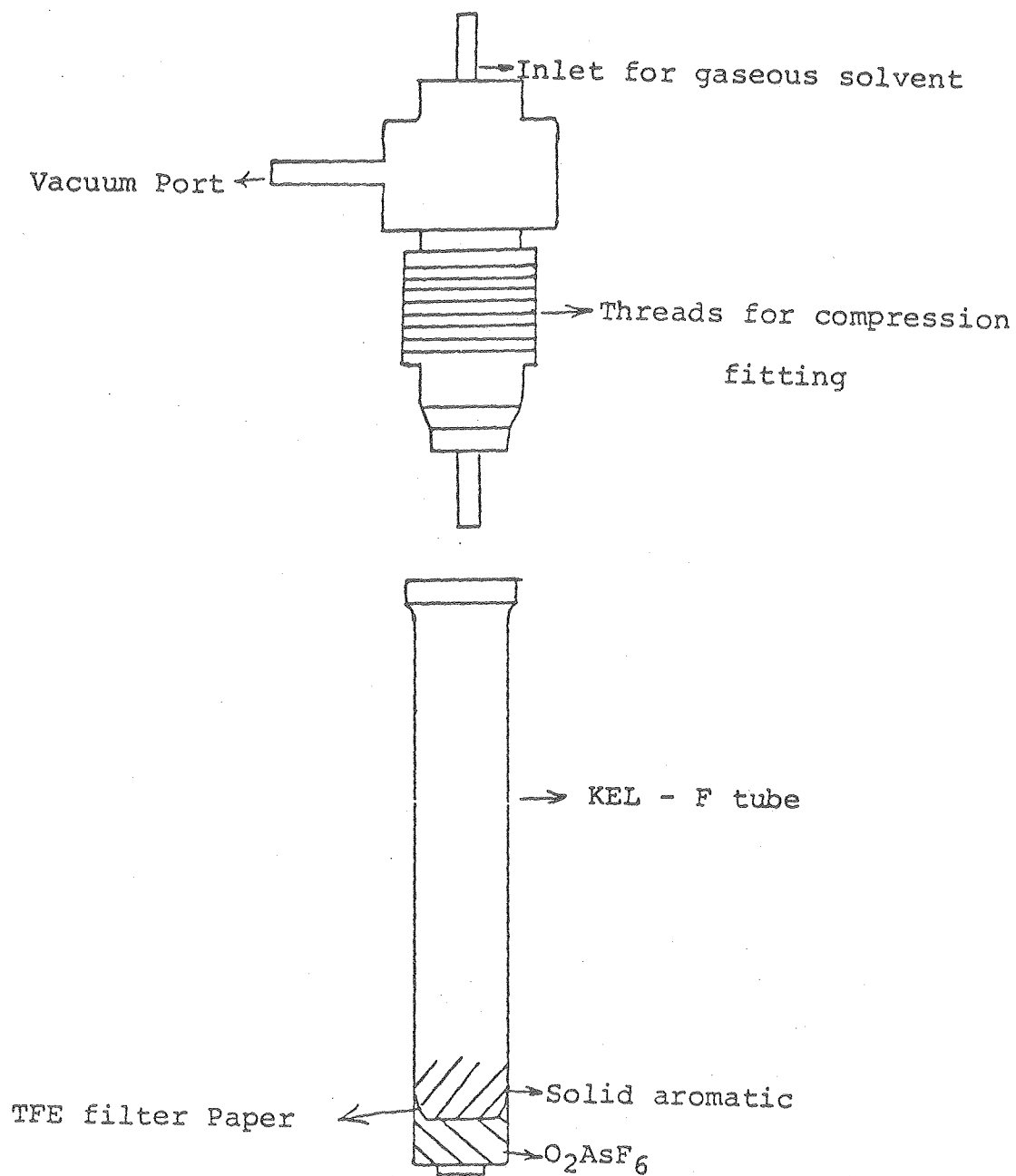


Figure II-1 Vessel for Solid-Solid Reactions

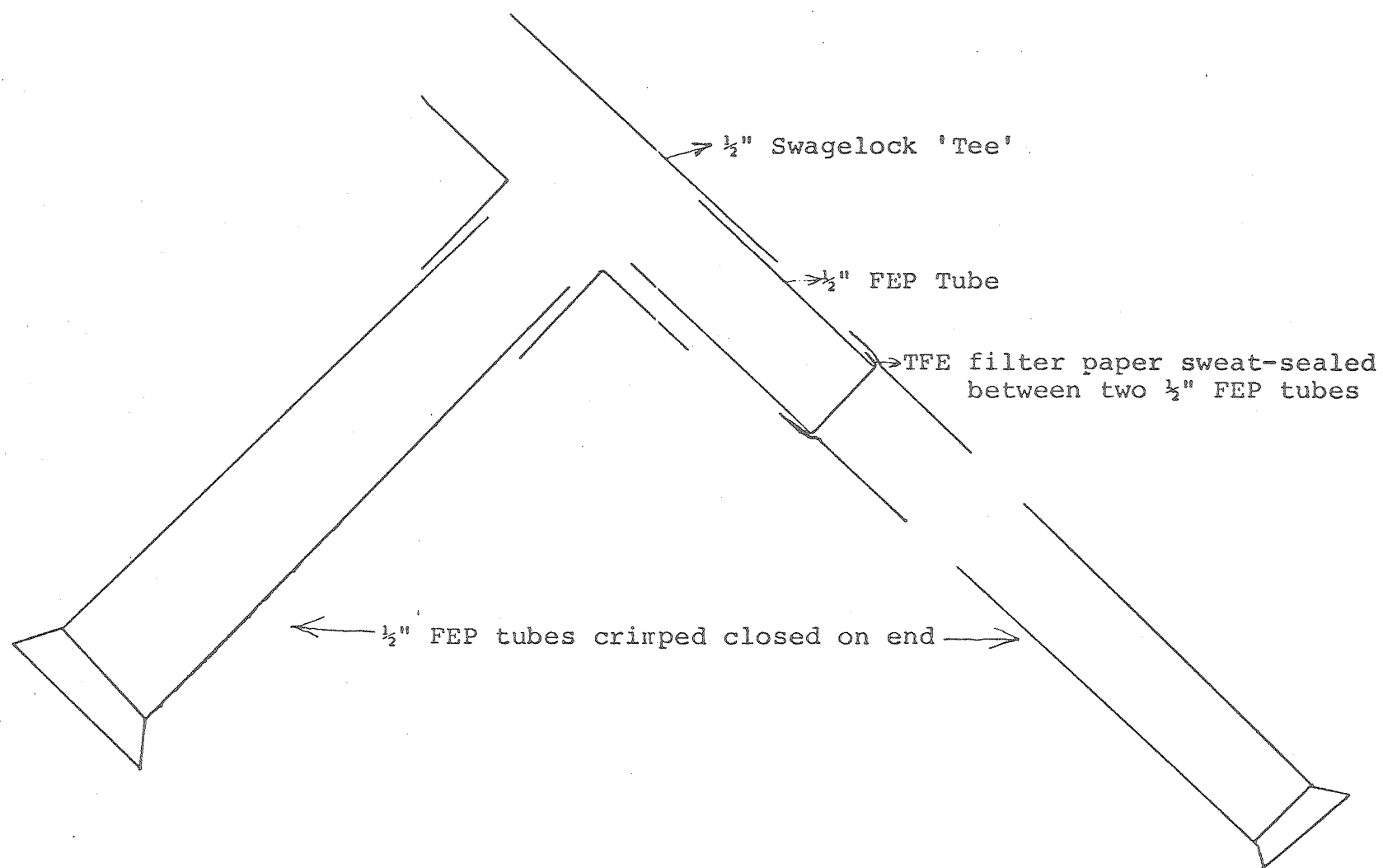


Figure II-2 Teflon Filtration Apparatus

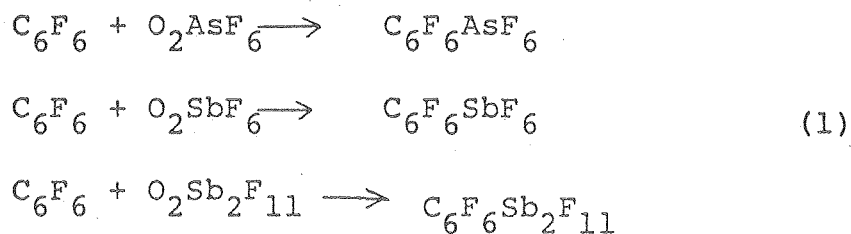
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III. OXIDATION PRODUCTS OF PERFLUOROAROMATICS

A. Introduction

Radical cations derived from a number of perfluoro- and polyfluoroaromatic molecules have been detected spectroscopically in superacid and oleum solutions.¹⁻⁵ Moreover, such species have been proposed as intermediates in the oxidative fluorination of aromatic systems by high-valent metal fluorides,⁶ bromine trifluoride⁷ and xenon difluoride,⁸ as well as in electrochemical fluorinations in the presence of fluoride ions.⁹ Salts of these radical cation species were unknown prior to the synthesis¹⁰ of salts of the hexafluorobenzene cation, $C_6F_6^+$ in these laboratories. In those studies dioxygenylhexafluoroarsenate (V) and -fluoroantimonates(V) were used as the oxidizers:



This technique has been extended by utilizing the solvent SO_2ClF , the low melting point of which has made possible the synthesis of less thermally stable perfluoroaromatic radical cation salts. Here we report additional structural and chemical information on $C_6F_6^+AsF_6^-$, and the preparation and characterization of salts of octafluoronaphthalene, octafluorotoluene and pentafluoropyridine. These studies have been limited by the low thermal stability of the salts of the single-ring aromatics. However, their

decomposition involves oxidative fluorination of the cation to give an equimolar mixture of the parent fluorocarbon and the appropriately substituted cyclohexadiene, for example



Since the initial product diene has proved to be a specific isomer, it appears that these reactions are kinetically controlled. For the preparation of such cyclohexadienes, these salts provide clean high-yield syntheses.

B. Results and Discussion

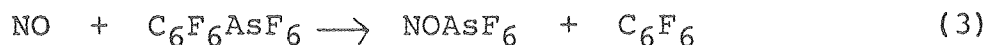
Characterization of the salts $\text{C}_6\text{F}_6\text{AsF}_6$ (I), $\text{C}_5\text{F}_5\text{NASF}_6$ (II), $\text{CF}_3\text{C}_6\text{F}_5\text{AsF}_6$ (III) and $\text{C}_{10}\text{F}_8\text{AsF}_6$ (IV) derives from a combination of physical and chemical studies. The discussion of the characterization of I extends that presented earlier by Richardson.¹¹ Because of the thermal instability of all except IV, these studies have usually been carried out on salts contaminated by their thermal decomposition products.

The finding, in this work, that the low melting (-125°) compound SO_2ClF can be used as a solvent for C_6F_6 in its interaction with O_2AsF_6 :



Has resulted in improved yields, which have been as high as 80%, because of the low reaction temperature permitted by this solvent. Nevertheless even with samples prepared

at -40 there are indications that thermal decomposition products are present since the magnetic moment ($\mu_{\text{eff}} = 1.30$ B. M.) is lower than that anticipated. The obedience to a Curie Law and the g value of 2.0038 from broad-line ESR studies do however show that the salt is a simple paramagnet. Also, the approximately 1:1 interaction of the freshly prepared salt with nitric oxide according to the equation:



V

is in accord with the energetics and supports the salt formulation. Thus, from the known ionization potentials of NO (213 kcal/mole) and C_6F_6 (230 kcal/mole) and the estimated lattice energies of $\text{C}_6\text{F}_6\text{AsF}_6$ and NOAsF_6 (-110 and -125 kcal/mole respectively) the estimated enthalpy change for (3) is -32 kcal/mole.

Although no Raman data is available due to decomposition in the laser beam, the IR spectrum of $\text{C}_6\text{F}_6\text{AsF}_6$ is very simple, with ν_3 and ν_4 of AsF_6^- at 700 and 400 cm^{-1} respectively, a benzene ring stretching band at 1490 cm^{-1} (compared to 1530 cm^{-1} in C_6F_6) and a C-F stretching band at 1030 cm^{-1} (1019 cm^{-1} and 994 cm^{-1} in C_6F_6). These latter two bands, are significantly shifted from the parent fluorocarbon and hint that the C-C bonding is weakened and the C-F bonding strengthened due to oxidation. These spectra give no evidence for a distortion in the cation although

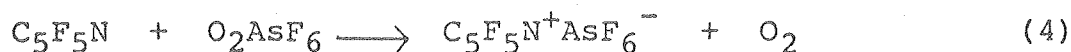
a distortion has been detected¹² recently in $C_6F_6^+$.

Single crystals of $C_6F_6AsF_6$ had been obtained by Richardson¹¹ by cooling HF solutions. Decompositions of the crystals in the X-ray beam prevented the collection of adequate data for a full structure determination, but the precession photographs and the partial diffractometer data indicated the space group to be $R\bar{3}$ with $a = 6.60(1) \text{ \AA}$, $\gamma = 106.0(1)^\circ$, and $V = 246.1 \text{ \AA}^3$. From the molecular volume of C_6F_6 (142 \AA^3) and AsF_6^- (105 \AA^3), the volume is seen to be consistent with one molecule per formula unit.

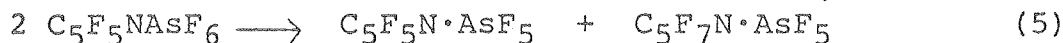
$C_6F_6AsF_6$ decomposes at room temperature via reaction (2) to give an equimolar mixture of C_6F_6 and 1,4- C_6F_8 (VI), a cyclohexadiene. The ^{19}F NMR spectrum of these products is presented in Table III-1. A possible mechanism for this decomposition will be discussed later.

$C_5F_5N^+AsF_6^-$ (II) and $CF_3C_6F_5^+AsF_6^-$ (III) decompose much more readily than $C_6F_6AsF_6$. The greater lability prevented the gathering of magnetic susceptibility or crystallographic data, as well as the recording of infrared spectra. Decomposition in the laser beam prevented the recording of any Raman spectra. Therefore, II and III were characterized from gravimetric data on the syntheses, broad-line ESR spectra recorded on the salts, and spectral identification of the thermal decomposition products.

The interaction of O_2AsF_6 with measured aliquots of C_5F_5N :

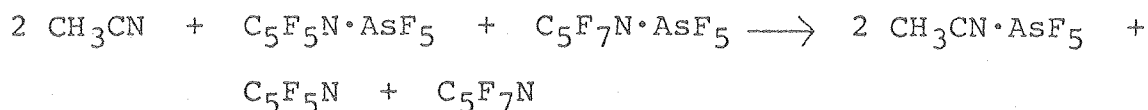


resulted in the evolution of equimolar amounts of O_2 and the formation of a deep-blue solid. The broad-line ESR g-value for the solid, of 2.0032, indicates that the salt is a simple paramagnet. Above 0° the blue solid changed into a colorless solid, the half-life at room temperature being a few minutes. The resulting diamagnetic colorless solid was shown by mass and vibrational spectroscopy to be a mixture of the two Lewis acid-base adducts:



The adduct $\text{C}_5\text{F}_7\text{N} \cdot \text{AsF}_5$ dissociates more readily than $\text{C}_5\text{F}_5\text{N} \cdot \text{AsF}_5$ and was removed from the latter by subjection of the solid to a dynamic vacuum. The $\text{C}_5\text{F}_5\text{N} \cdot \text{AsF}_5$ remaining was identified by comparison of its Raman and IR spectra with those of a 1:1 adduct prepared tensimetrically by direct interaction of $\text{C}_5\text{F}_5\text{N}$ and AsF_5 (see Table III-2).

Since acetonitrile is a good Lewis base, it dissolved the two adducts, from the preparation mixture, to liberate the parent bases:



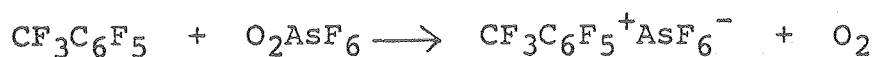
Dissolution of the mixture of adducts formed on warming the $\text{C}_5\text{F}_5\text{NASF}_6$ salt to room temperature gave a colorless solution ^{19}F NMR spectra of which established $\text{C}_5\text{F}_5\text{N}$ and $\text{C}_5\text{F}_7\text{N}$ to be present in equimolar proportions. The ^{19}F NMR spectra

(presented in Table III-3) also established that the sole C_5F_7N isomer was heptafluoro-1-azacyclohexa-1,3-diene (VII)



VII

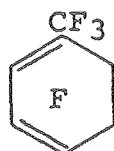
The preparation of the yellow-green salt $CF_3C_6F_5 AsF_6^-$ was essentially the same as for $C_6F_6^+ AsF_6^-$:



Again, the broad-line ESR spectrum ($g = 2.018$) indicates that the salt is a simple paramagnet but the greater lability of this salt frustrated attempts at meaningful bulk susceptibility measurements. The thermal decomposition of $CF_3C_6F_5 AsF_6$ proceed according to the equation:



The equimolar mixture of $CF_3C_6F_5$ and the cyclohexadiene $CF_3C_6F_7$ was established by the ^{19}F NMR spectrum (presented in Table III-4). These spectra also established that the initial cyclohexadiene product was 1-(trifluoromethyl)-heptafluorocyclohexa-1,3-diene (VIII).



VIII

Since $C_{10}F_8^+AsF_6^-$ is stable to above 100° it has been characterized by its physical and chemical properties.

The synthesis from $C_6F_6AsF_6$:



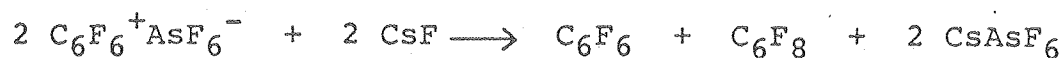
in quantitative, based on $C_{10}F_8$. ESR, vibrational and electronci spectra are all consistent with the species characterized¹³ as $C_{10}F_8^+$ in super-acid solution. Magnetic susceptibility measurements were made on several different preparations. The data (Figure III-1) show that the salt obeys the Curie Weiss law over the temperature range $5 - 80^\circ$ K with a Weiss constant of -0.8° . The value of the magnetic moment varied slightly from sample to sample and probably means that the samples were contaminated by $C_{10}F_8$. Nevertheless, the simple magnetic behavior indicates a magnetically dilute system and the minimum observed moment of $\mu_{eff} = 1.68$ B. M. indicates a doublet species.

Attempts were made to grow single crystals of $C_{10}F_8AsF_6$ from SO_2 solution, in which the salt is freely soluble, but no crystals were obtained and moreover the powder photograph of the solid, obtained on removal of the solvent, did not coincide with that of the starting material. Presumably the salt forms an SO_2 solvate, although this was not established. All other attempts to grow crystals failed but the X-ray powder pattern was indexed on the basis of a tetragonal unit cell with $a = 8.24$, $b = 18.44$ A, $V = 1252$ Å³.

The data and its indexing are presented in Table III-5. The

volume of this cell indicates four formula units/cell since the volume¹⁴ of a $C_{10}F_8$ molecule (from crystallographic studies) is 226 \AA^3 and $V_{AsF_6^-} = 105 \text{ \AA}^3$. It is also encouraging that the dimensions of the unit cell have a simple relationship to the dimensions of the $C_{10}F_8$ molecule as represented in the Figure III-2. This figure also shows the proposed arrangement of the $C_{10}F_8^+$ and AsF_6^- species in the unit cell. Such an arrangement is dictated by the cation shape, the need to separate ions of like charge to the greatest extent possible (within the limitations imposed by the need for close packing) and the tetragonal symmetry. This model is highly satisfactory. Each cation is coordinated by four anions such that each of the two rings of the cation is close to two anions, one above and one below the plane of the ring. Thus, at least in the solid salt the positive hole of the cation is shared equally between the two rings.

The products of the thermal decomposition of the single-ring radical cation salts (e.g. Reaction 2) indicates that at least the first step in the decomposition of each salt involves F^- transfer from anion to cation. In accordance with this notion, the reaction of $C_6F_6AsF_6$ with Cs^+F^- in HF solution¹¹ yields products similar to those seen from the pyrolysis of the salt:



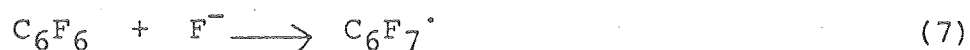
The most interesting feature of these fluoride ion

transfer decomposition reactions is the specificity of the diene product. The ^{19}F NMR studies show unambiguously that the dienes produced initially from the single-ring cation salts are VI, VII and VIII.



In the case of the perfluorotoluene salt a slow isomerization of the initial diene product occurs and the ^{19}F NMR spectra (see Table III-4) show the isomer IX appearing as the concentration of VIII declines. After three days spectra show that half of VIII has isomerized into IX. The sum of the integrated intensities from the CF_3 resonances of VIII and IX is equal to that of the CF_3 resonance from $\text{CF}_3\text{C}_6\text{F}_5$ in the final mixture. This isomerization is not reported in published studies¹⁵ of the synthesis and characterization of VIII or IX. The presence of the Lewis acid AsF_5 in the sealed NMR tube probably catalyses the isomerization.

Any theoretical model must account for the unique diene isomer of reactions 2, 5 and 6. It is reasonable to assume that the first step involves attack on the cation by F^- which has detached from the AsF_6^- ion. Thus C_6F_6^+ will yield C_6F_7 radical:



The production of half a mole of the parent aromatic in all the single-ring cases suggests that the next step involves the oxidation of this radical by a second mole of radical cation:

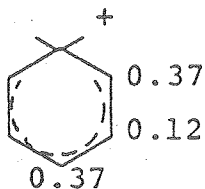


The diene is probably formed by F^- attack on the cation formed:



The uniqueness of the diene product of course requires that the rate of the F^- attack in each case be specific. For the hexafluorobenzene case we need only consider the second F^- attack.

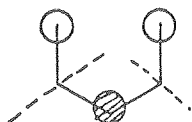
It appears that charge distribution in the cation does not by itself determine the attack site. This is illustrated by the C_6F_7^+ species. The charge distribution has been calculated by Clark and his coworkers⁶ and is shown below:



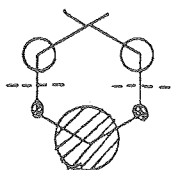
Since the only diene produced is the 1,4 diene it is apparent (even allowing for some unreliability in these numbers) that charge distribution considerations cannot, by themselves, account for the product.

It is likely that the choice of F^- attack site is in each case determined by the best overlap of the F^- HOMO with

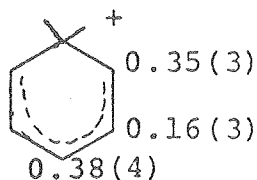
the cation LUMO. The $C_6F_7^+$ species can be viewed as a perturbed pentadienyl radical. The LUMO of the pentadienyl radical is as shown:



The endocyclic CF_2 is anticipated to have the impact of moving the nodes towards the CF_2 group. The sizes of the resulting orbital coefficients are qualitatively illustrated below:



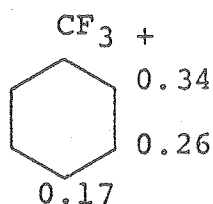
The spin densities calculated for $C_6F_7^+$ by Clark and his coworkers⁶ are given below



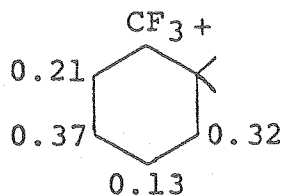
The difference between position 2 and position 4 does not appear to be large enough and this may simply be a consequence of difficulties inherent in such calculations.

Although these results predict attack to occur primarily at site 4 (with minor products resulting from attack at site 2), the stereospecificity of the products require exclusive preference for site 4, suggesting that the coefficient for carbon atom 4 is much larger than reported.

The perfluorotoluene case is more complex. The uniqueness of the diene product requires that the interaction of F^- with $CF_3C_6F_5^+$ must also be totally specific as to which C atom is attacked initially by F^- . Again, charge density calculations have been carried out and those of Burdon and Parsons¹⁶ are shown below

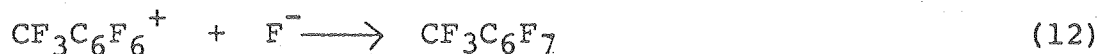
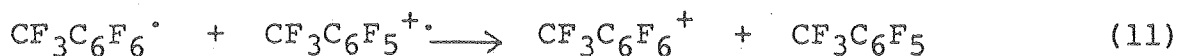
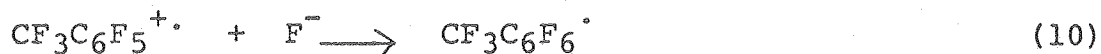


This predicts a preference for attack at the ortho C but the cation derived therefrom has the charge distribution:

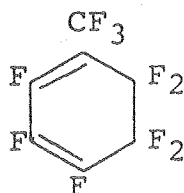


This narrowly favors the initial formation of a 1,3 diene in equation 12 which is not observed experimentally.

Again, it is necessary to consider the qualitative description of the LUMO's in order to be consistent with the proposed mechanism:

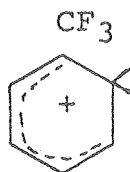


Since the diene initially observed from this reaction is VIII:

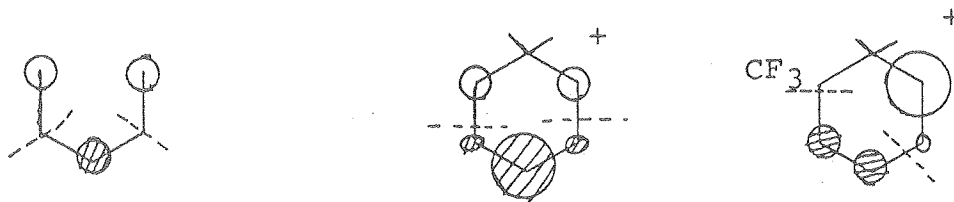


VIII

it is probable that reaction 10 involves attack at the ortho position since the $\text{CF}_3\text{C}_6\text{F}_6$ radical product and the subsequent cation formed is most likely to yield VIII. This $\text{CF}_3\text{C}_6\text{F}_6^+$ cation:

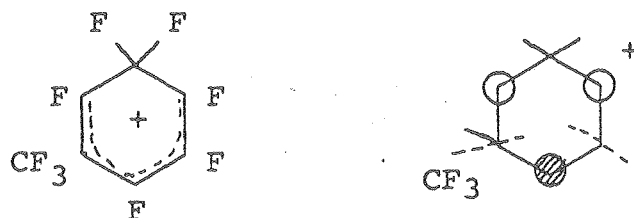


may be viewed as a perturbed pentadienyl radical. The impact of the endo CF_2 group of the ring has already been noted. The inductive influence of the exocyclic CF_3 group must also be large. The effect proposed is illustrated below:

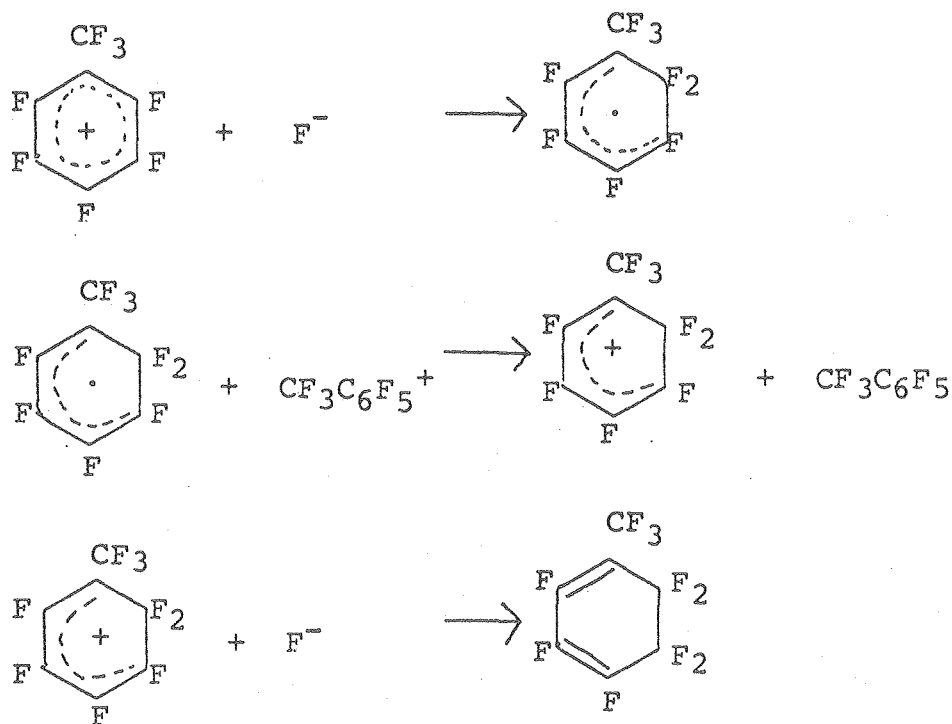


Obviously, F^- attack on the carbon with the largest coefficient will yield VIII.

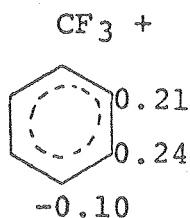
If the initial cation attack occurs at the meta position; the LUMO for the $\text{CF}_3\text{C}_6\text{F}_6^+$ formed would be as shown below:



Qualitatively it is difficult to discriminate between the 2, 4 and 6 sites for the F^- attack and it therefore seems more likely that if this were the cation intermediate a mixture of dienes would be produced. On balance then, it seems more likely that the perfluorotoluene cation is attacked first in the ortho position:

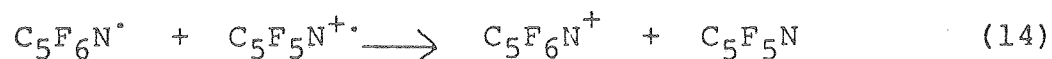
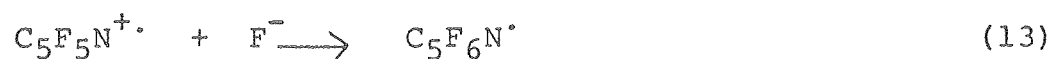


The spin densities for $CF_3C_6F_5^+$ have been reported by Burdon and Parsons¹⁶:

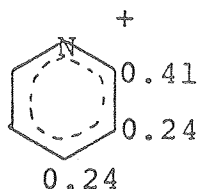


These data predict that F^- attack in equation 10 will occur primarily at the meta position with some attack occurring at the ortho position. This would result in the $CF_3-C_6F_7^+$ formed consisting of a mixture of isomers. This is not in harmony with the formation of one diene isomer in equation 12 and therefore cannot properly predict the experimentally observed products.

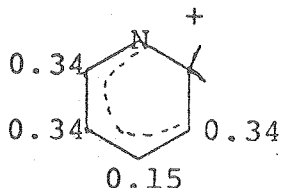
The analogous mechanism for pyrolysis of $C_5F_5NAsF_6$ by F^- attack on the cation is given below:



As in the perfluorotoluene case, isomer specific products must be formed in both the first reaction (13) and the third (15). Charge density calculations have been reported by Clark and coworkers⁶ and are shown below:

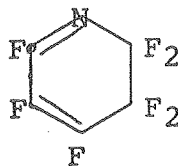


This predicts a preference for attack at the ortho carbon atom but the cation subsequently derived from such attack has the charge distribution given below:



F^- attack on this cation via equation 15 would give a mixture of 1,3- and 1,4-dienes not seen experimentally.

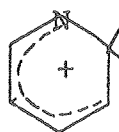
The qualitative description of the LUMO's for pentafluoropyridine is quite similar to that for perfluorotoluene. This is reassuring since the diene exclusively produced in this reaction VII is completely analogous to that found initially in the perfluorotoluene case:



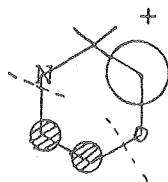
VII

Since the endocyclic N atom will lend approximately the same inductive effect to the unperturbed LUMO's as shown earlier for the exocyclic CF_3 group, the qualitative illustration of the orbital coefficients will be essentially the same.

Therefore F^- attack on the ortho carbon of $C_5F_5N^+$ in reaction 13 would give the following isomer of $C_5F_6N^+$ to react in equation 15:



Since the inductive effects are nearly the same, the LUMO for this cation would be analogous to that for the corresponding perfluorotoluene isomer and is shown below:

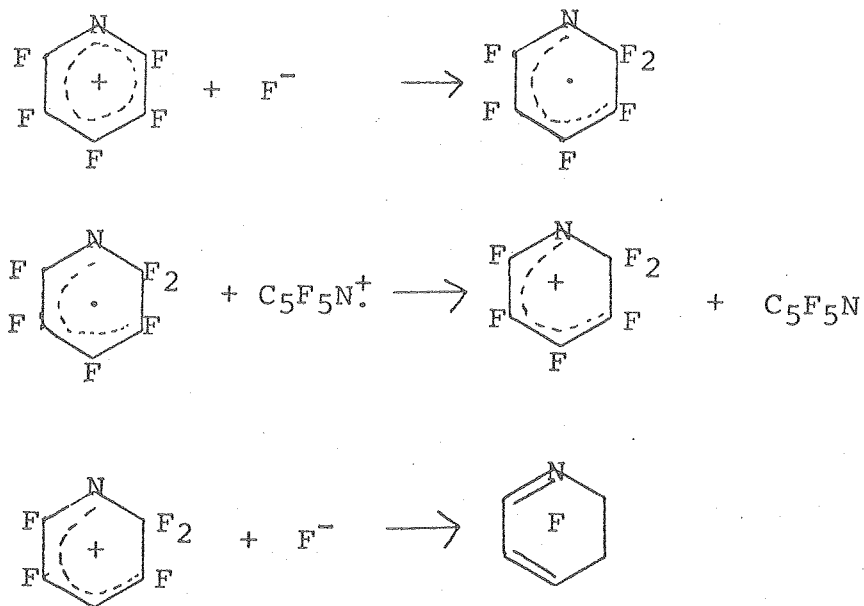


F^- attack on the carbon with the largest coefficient will yield VII.

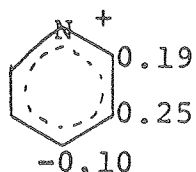
Analogously, if the fluoride ion were to attack on the meta position of $C_5F_5N^+$ in reaction 13 the cation subsequently formed to reaction 15 would have the LUMO shown below:



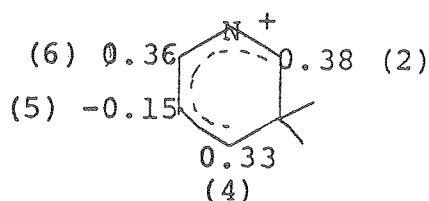
as in the perfluorotoluene case, this predicts that F^- attack in equation 15 would lead to a mixture of C_5F_7N isomer which is not observed experimentally. Therefore, pyrolysis of $C_5F_5NAsF_6$ through F^- attack should proceed as follows:



Clark and coworkers have reported the spin densities for $C_5F_5N^+$:

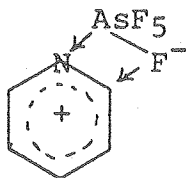


This predicts that F^- will attack preferentially at the meta position to give the isomer of $C_5F_6N^+$ for which the following spin densities have been calculated:



F^- ion would be expected to attack at positions 2, 4 and 6 (with only a slight preference for position 2) to give a mixture of diene isomers. Again, this is not in agreement with the qualitative picture developed above and does not predict the experimentally observed results.

It is noteworthy that the diene formed from the pyrolysis of $C_5F_5NAsF_6$ occurs initially as the adduct $C_5F_7N \cdot AsF_5$ (as does the pentafluoropyridine: $C_5F_5N \cdot AsF_5$). It is possible that the F^- attacking the cations could be in the form of AsF_6^- with the AsF_5 directing the point of F^- attack via interaction with the N, ie:

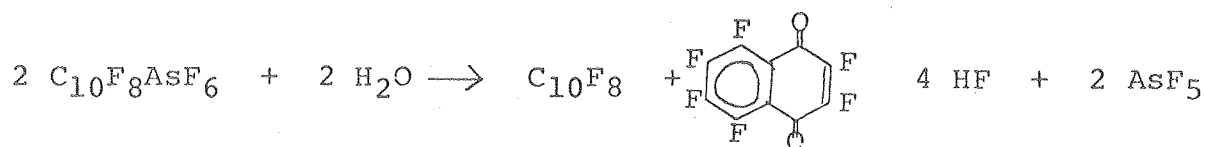


This could at least account for the preference of initial attack at the ortho position.

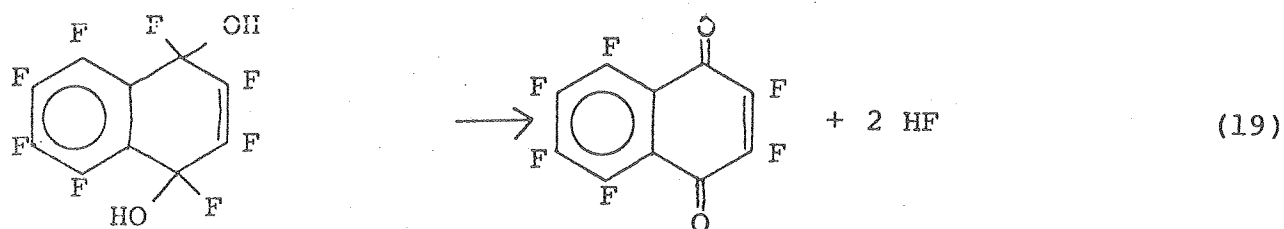
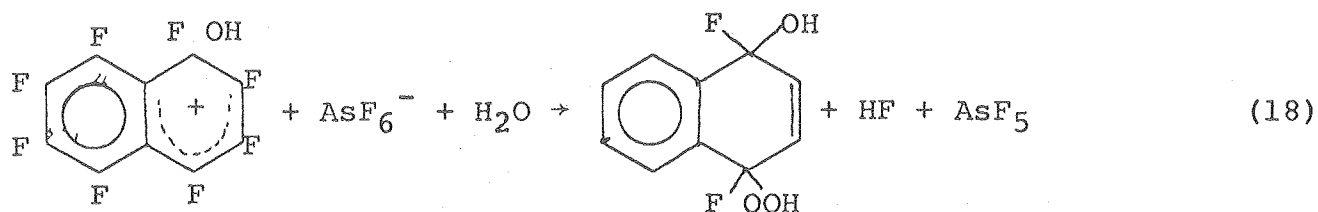
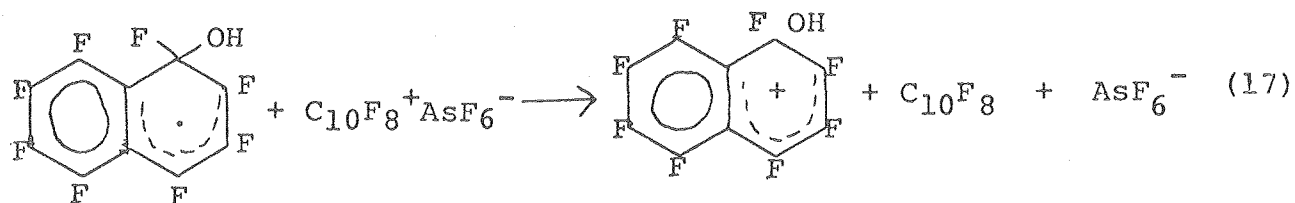
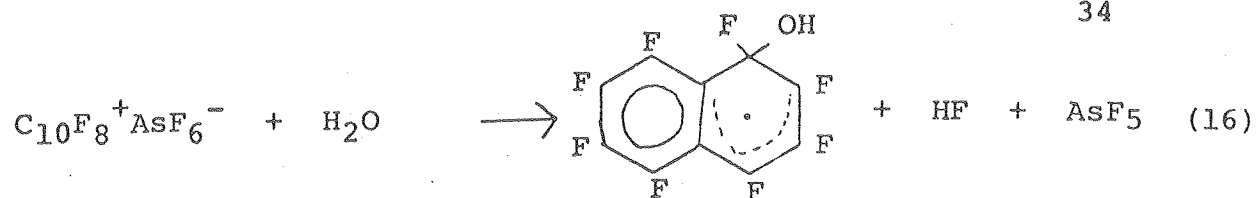
It is also noteworthy that in the diene VII, formed from $C_5F_5NASF_6$, the N atom maintained its double bond to carbon. The same is true about the CF_3 -substituted C atom in VIII. It may be important to maintain the π -delocalization through these bridgehead atoms and therefore influence the formation of the observed diene isomer.

When $C_{10}F_8AsF_6$ is reacted with F^- (as CsF) in HF a colorless solid is formed. The ^{19}F NMR spectrum (Figure III-3) shows the product to consist mainly of $C_{10}F_8$ with a very small amount of 1,4- $C_{10}F_{10}$ and some other unidentified products. Since this unexpected result does not aid in the characterization of $C_{10}F_8AsF_6$, the salt was reacted with water as an OH^- source. It was hoped that this would form a equimolar mixture of $C_{10}F_8$ and $C_{10}F_8(OH)_2$.

$C_{10}F_8AsF_6$ reacts with water according to the following reaction:

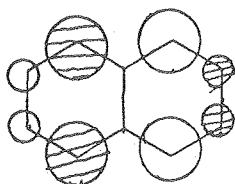


The formation of an equimolar mixture of octafluoronaphthalene and 1,4-naphthoquinone is documented by the ^{19}F NMR spectrum (Figure III-4). The mechanism for this hydrolysis probably proceeds as follows:



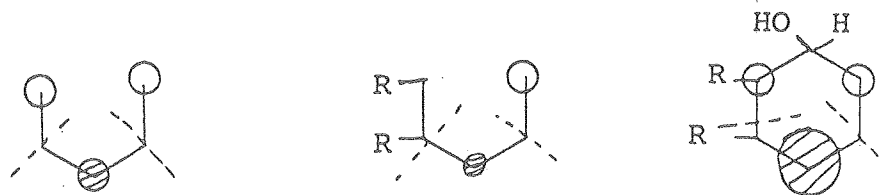
Hence OH^- attack or $\text{C}_{10}\text{F}_8^+$ proceeds in an analogous fashion to F^- attack on the single ring aromatics.

The stereo specificity of the quinone formation is similar to that for the formation of the cyclohexadienes described above. The attack of OH^- on the α carbon in (16) can be justified by assuming that the HOMO for $\text{C}_{10}\text{F}_8^+$ is similar to that calculated for naphthalene:¹⁷



Since the orbital on the α carbon is the largest the OH^- would be expected to attack at that position.

The HOMO of the intermediate formed after oxidation in (17) can be viewed as that of a substituted pentadienyl radical as has been done in earlier cases:



The effect of the HCOH group is to draw the nodes towards itself, thus causing the orbital on the opposite carbon to be the largest in the HOMO. Hence, the second OH^- will attack at C_4 (as shown in 18) to give 1,4-Naphthoquinone after HF elimination. Spin-densities and charge-densities have not been reported for cation and radical intermediates in this system.

C. Experimental

1. Preparation of $\text{C}_6\text{F}_6^+\text{AsF}_6^-$

Onto O_2AsF_6 (0.635 g, 2.87 mmol) was condensed 1.5 ml SO_2ClF followed by an excess of C_6F_6 and another 0.5 ml of solvent at -196° . Upon warming, the reaction began as soon as the solvent melted and went to completion (O_2 evolution ceased) at -40° . After removing all volatiles at the reaction temperatures the solid was briefly pumped to dryness at room temperature. The golden-yellow product (0.86 g, 2.29 mmole) was stored in the vessel at -78° . The yield was often lower and averaged $\sim 60\%$.

Magnetic susceptibility measurements after the manner already described by Richardson¹¹ yielded $\mu_{\text{eff}} > 1.3$ B.M. The ESR spectrum (powder) gave a broad symmetric resonance at $g = 2.0038$. No high resolution spectra were ever obtained. The IR spectrum agreed with that previously given by Richardson¹¹.

2. Thermal decomposition of $\text{C}_6\text{F}_6^+\text{AsF}_6^-$

After 3 hours at room temperature a sample of freshly prepared $\text{C}_6\text{F}_6^+\text{AsF}_6^-$ had decomposed to colorless products. Dry CH_3CN was condensed onto the products to form the adduct with AsF_5 ,⁹ and the remaining volatiles were condensed into an NMR tube containing a small amount of CF_3COOH . The tube was sealed. The ^{19}F NMR spectrum of this system established the presence of C_6F_6 and the 1,4 diene C_6F_8 in essentially 1:1 molar ratio as documented in Table III-1. The IR spectra of the volatiles were similarly compatible with such a mixture and have been described previously by Richardson.¹¹

3. Interaction of $\text{C}_6\text{F}_6\text{AsF}_6$ with NO

To a tube containing freshly prepared $\text{C}_6\text{F}_6^+\text{AsF}_6^-$ (0.656 mmoles) NO gas was admitted slowly, and not in excess until the reaction had gone almost to completion. The color of the C_6F_6^+ disappeared quickly and C_6F_6 was liberated. Raman and X-ray powder photography showed that the solid product was $\text{NO}^+\text{AsF}_6^-$ (0.639 mmoles).

4. Synthesis and Thermal Decomposition of $\text{CF}_3\text{C}_6\text{F}_5^+\text{AsF}_6^-$

$\text{CF}_3\text{C}_6\text{F}_5$ has been reacted with O_2AsF_6 to form

$\text{CF}_3\text{C}_6\text{F}_5\text{AsF}_6$ in a similar manner to that described for $\text{C}_6\text{F}_6\text{AsF}_6$. The lime-green solid decomposed more quickly at room temperature than the C_6F_6^+ salt but could be preserved indefinitely at -45° . After $\text{CF}_3\text{C}_6\text{F}_5\text{AsF}_6$ had decomposed to colorless products (one hour at room temperature) ^{19}F NMR spectra were obtained in essentially the same fashion as for $\text{C}_6\text{F}_6\text{AsF}_6$ and are presented in Table III-4. It is shown that the initial decomposition products are octafluorotoluene and 1-(trifluoromethyl)heptafluorocyclohexa-1,3-diene in a 1:1 molar ratio. With time, the latter is converted to an equilibrium mixture ($\sim 1:1$) with its isomer 1-(trifluoromethyl)heptafluorocyclohexa-1,4-diene.

5. Synthesis and Thermal Decomposition of $\text{C}_5\text{F}_5\text{NAsF}_6$

$\text{C}_5\text{F}_5\text{N}$ has been reacted with O_2AsF_5 to form $\text{C}_5\text{F}_5\text{NAsF}_6$ in a similar manner to that described for $\text{C}_6\text{F}_6\text{AsF}_6$. The blue solid also decomposed quickly at room temperature to a colorless solid but could be preserved indefinitely at -25° . After $\text{C}_5\text{F}_5\text{NAsF}_6$ had decomposed to colorless products (one hour at room temperature) ^{19}F NMR spectra were obtained in essentially the same fashion as for $\text{C}_6\text{F}_6\text{AsF}_6$ and are presented in Table III-3. It is shown that the initial decomposition products are pentafluoropyridine and 1-azaheptafluorocyclohexa-1,3-diene in a 1:1 molar ratio. IR and Raman spectra on the colorless solid are presented in Table III-2 and show the presence of the $\text{C}_5\text{F}_5\text{NAsF}_5$ adduct.

6. Synthesis of $\text{C}_5\text{F}_5\text{N}\cdot\text{AsF}_5$

AsF_5 was condensed onto $\text{C}_5\text{F}_5\text{N}$ in a quartz tube at

-196. Upon warming towards room temperature the white solid $C_5F_5N \cdot AsF_5$ formed in the tube. The Raman spectrum is presented in Table III-2.

7. Preparation of $C_{10}F_8^+AsF_6^-$

O_2AsF_6 (1 g, 4.5 mmole) was reacted with C_6F_6 as described above, except that the product was stored at -196 with the solvent present. The tube was quickly transferred to a dry nitrogen-filled glove bag provided with a metal finger which could be cooled externally. The reaction tube was placed in the finger and cooled to -196° . The vessel was opened and $C_{10}F_8$ (0.62 g, 2.3 mmole) was added. After quickly closing it the vessel was returned to the vacuum line, cooled once more to -196° , evacuated, and warmed to -40° for 30 minutes. The tube was shaken to ensure mixing of the reactants and the yellow color characterization of $C_6F_6^+AsF_6^-$ quickly gave way to the dark green color of $C_{10}F_8^+AsF_6^-$. Volatiles were removed under vacuum as the vessel was warmed to 25° (causing the excess $C_6F_6AsF_6$ to decompose). Removal of all volatiles gave a free-flowing dark-green solid (1.08 g, 2.3 mmole; mp = 122 ± 3). Anal. Calcd for $C_{10}F_8AsF_6$: C, 26.1. Found: C, 26.1.

Magnetic susceptibility measurements were made on several different samples. The data which is considered most reliable is presented in Figure III-1. Vibrational data for $C_{10}F_8AsF_6$ are given in Table III-7 along with the comparable data for $C_{10}F_8$ and AsF_6^- . These findings support the $C_{10}F_8^+AsF_6^-$ formulation.

X-ray powder patterns were relatively simple and were indexed on the basis of a tetragonal cell with $a = 8.24(1) \text{ \AA}$, $c = 18.4(1) \text{ \AA}$ and $V = 1249 \text{ \AA}^3$. The indexing is presented in Table III-5.

8. Hydrolysis of $C_{10}F_8AsF_6$

$C_{10}F_8AsF_6$ ($\sim 0.5 \text{ g}$) was reacted with an excess of H_2O in the presence of $5 \text{ ml } CCl_4$ to give a yellow solid. The ^{19}F NMR spectrum (in a 1:1 CH_3OH/C_6H_6 mixture) is presented in Figure III-4 and indicates a mixture of $C_{10}F_8$ and 1,4-Napthoquinone in a 1:1 molar ratio.

9. Interaction of $C_{10}F_8AsF_6$ with CsF

$C_{10}F_8AsF_6$ ($\sim 0.25 \text{ g}$) was mixed with an excess of CsF in HF until no green color persisted (approximately one hour). The ^{19}F NMR spectrum were obtained in essentially the same fashion as for the pyrolysis products of $C_6F_6AsF_6$ and is shown in Figure III-3. The spectrum consists mainly of $C_{10}F_8$ with a small amount ($\sim 5\%$) of decafluoro-1,4-dihydro-naphthalene.

Table III-1 ^{19}F NMR Data for Decomposition Products of $\text{C}_6\text{F}_6\text{AsF}_6$

<u>Shift ^a(Rel. Intensity)</u>	<u>C_6F_6 ^b</u>	<u>1,4 C_6F_8 ^b</u>
-114.9(2)		-115
-159.7(2)		-160
-166.5(3)	-165	

a) Negative sign refers to ppm upfield of CFCl_3

b) C-H. Dungan and J. R. VanWazer, "Compilation of Reported ^{19}F NMR Chemical Shifts", Wiley-Interscience, New York (1969).

Table III-2 Raman Data for Decomposition Products of
 $\text{C}_5\text{F}_5\text{NASF}_6$

<u>cm^{-1} (Rel. Intensity)</u>	<u>$\text{C}_5\text{F}_5\text{N}\cdot\text{AsF}_5$ cm^{-1} (Rel. Intensity)</u>
175(6)	
	225(3)
280(5)	285(5)
296(6)	
303(7)	304(4)
342(16)	
353(6)	348(3)
363(6)	
386(10)	
392(10)	
401(20)	
408(9)	409(18)
438(10)	
448(24)	453(21)
486(7)	490(8)
504(5)	
590(69)	596(58)
638(7)	643(7)
647(17)	
663(58)	668(37), 673(5)
706(12)	
715(11)	720(7)
730(11)	
738(9)	
743(8)	
	754(3)

Table III-3 ^{19}F NMR Data of Decomposition Products of $\text{C}_5\text{F}_5\text{NASF}_6$ (in CH_3CN)

<u>Shift^a (Rel. Intensity)</u>	<u>$\text{C}_5\text{F}_5\text{N}^b$</u>	<u>$1,3\text{-C}_5\text{F}_7\text{N}^{c,d}$</u>
- 43.6(1)		- 45.6(1)
- 87.6(2)	- 87.6(2)	
-101.4(2)		- 99.6(2)
-123.2(2)		-121.6(2)
-134(1)	-134.2(1)	
-140.5(1)		-140.7(1)
-151.9(1)		-150.5(1)
-162(2)	-162.0(2)	

a) Negative sign refers to ppm upfield of CFCl_3 .

b) R. D. Chambers, J. H. Hutchinson and W. K. R. Musgrave,
J. Chem. Soc., 1964, 3573. (neat)

c) Reference 6.

d) 1-azaheptafluorocyclohexa-1,3-diene. (neat)

Table III-4 ^{19}F NMR Data for Decomposition Products of $\text{CF}_3\text{C}_6\text{F}_5\text{AsF}_6$ (in CH_3CN)

<u>Shift^a, (Rel. Intensity, Multiplicity)</u>		<u>$\text{CF}_3\text{C}_6\text{F}_7$ assignment (see below)</u>	
<u>Initial Products</u>	<u>After 3 days</u>	<u>$\text{CF}_3\text{C}_6\text{F}_5^b$</u>	
- 56.7(3, t)	- 56.7(6, t)	56.0(3, t)	
- 58.8(3, dt)	- 58.4(3, t)		F ₁ F _a
-104.1(2, m)	- 58.8(3, dt)		F ₂
	-104.1(2, m)		
	-110.0(1, m)		F ₃ F _f
-113.5(2, quartet)	-113.5(2, quartet)		
-114.9(1, m)	-114.9(1, m)		F ₆
	-118.2(2, m)		
	-125.4(2, t)		F ₆ F _e
-140.5(2, m)	-140.5(4, m)	-140.0(2, m)	
-149.0(1, t)	-149.0(2, t)	-147.9(1, t)	
	-150.4(1, quartet)		
	-152.1(1, t)		F ₅ F _c
-153.2(1, septet)	-153.2(1, septet)		
-159.0(1, m)	-159.0(1, m)		F ₄ F _d
-161.7(2, dd)	-161.7(4, dd)	-160.6(2, dd)	

a) Negative sign refers to ppm upfield of CFCl_3 (in CFCl_3).

b) I. J. Lawrenson, J. Chem. Soc., 1965, 1117.

Table III-4 Contd.

Coupling Constants (Hz)

J_{12}	J_{13}	J_{15}	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	J_{36}	J_{45}	J_{56}
10	2	<1	22	10	21	5	21	4	10	4	2
J_{ab}	J_{ac}	J_{af}	J_{bc}	J_{bf}	J_{cd}	J_{ce}	J_{de}	J_{df}	J_{ef}		
2	2	7	13	3	17	2	20	3	17		

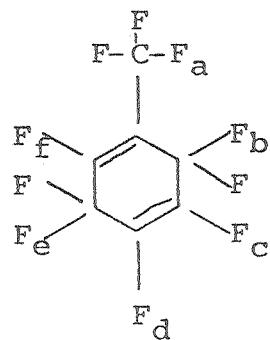
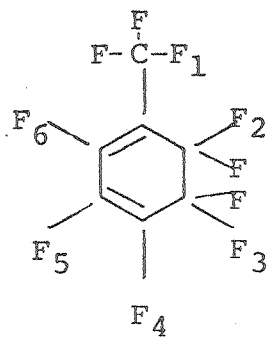


Table III-5 Powder Pattern of $C_{10}F_8AsF_6$ (Film No. 1241)

Tetragonal: $a = 8.24(1)$, $c = 18.44(9)$ Å, $V = 1252$ Å³ ($z = 4$)

<u>hkl</u>	<u>d_{hkl}</u>	<u>104/d² (obs.)</u>	<u>10⁴/d² (calc.)</u>	<u>Rel. Intensity</u>
100	8.23	148	147	S
101	7.52	177	176	S
	7.01	204		VW
102, 003	6.17	263	265, 265	W
110	5.79	298	295	VW
111	5.53	327	324	S
	5.16	376		W
103, 112	4.94	409	412, 413	VS
	4.67	459		M
113	4.23	558	560	S
201, 104	4.03	615	618	VS
202	3.77	703	707	VS
211	3.62	765	765	VS
	3.53	804		VVW
212, 203	3.43	852	854, 854	M
213	3.15	1007	1001	MW
220	2.91	1180	1178	W
222	2.76	1311	1296	VW
310	2.61	1472	1473	VW
312, 303	2.52	1581	1591	M
224	2.47	1642	1649	W
321	2.27	1937	1943	VW
322	2.22	2034	2032	VW
323	2.15	2166	2179	MW
401	2.05	2379	2385	MW
330	1.94	2647	2651	VW

Table III-6 Infrared Data for Decomposition Products of $C_6F_6AsF_6$

cm^{-1} (Rel. Intensity)	$C_6F_6^a$	1,4 $C_6F_8^b$	AsF_5^c
784 s			785
809 s			809
	849 w		
	868 w		
	883 w		
975 s		977 s	
1000 vs	1002 vvvs		
1020 vs	1020 vvvs	1023 s	
1045 sh	1044 mw		
1095 s	1092 m	1096 s	
1135 w		1130 w	
1195 w		1200 w	
1240 m		1240 ms	
	1259 w		
	1257 w		
1326 s		1325 s	
1370 mw	1368 s	1375 w	
		1410 w	
	1439 vw		
1460 w	1463 m		
	1486 m		
	1513 w		
1530 s	1531 vvvs		
	1547 m		
	1560 m		
	1570 m		
	1601 m		
	1685 w		
	1699 w		
1740 m		1742 ms	
1760 sh	1763 s		

- a) D. Steele and D. H. Wiffen, Trans. Farad. Soc., 65, 369 (1959).
- b) J. C. Tatlow and R. Stephens, private communication.
- c) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd Edition, Wiley-Interscience, New York, 1970.

Table III-7 Vibrational Data for $C_{10}F_8AsF_6$

$C_{10}F_8AsF_6$		$C_{10}F_8^a$	
<u>IR</u>	<u>RAMAN</u>	<u>IR</u>	<u>RAMAN</u>
	164 w		166 mw
	190 w		
	284 w		291 m
			301 sh
		317	
	331 w		339 mw
	382 m		375 vs
	396 m		394 w, sh
	420 vvs	405 m	
434 w	432 sh		432 vw
	517 ms		512 s
	540 w, hr	531 mw	528 vw
	580 w		577 vw
			601 mw
	646 s		642 vw
675 w, sh		670 mw	
697 ν_3 AsF_6^-	750 m		758 m
790 s	784 mw, 792 ms	784 s, 803 w, sh	
			859 vw
940 vw		946 s	
977 s		970 vw	
		1022	
		1044	
			1071 w
	1097 mw		1083 vw
1118 vw	1122 m	1120 s	
1135 w		1145 vw	
1170 s		1160 w	
		1203 s	1198 w
1245 s			1236 w
		1260 w	1280 w
		1291 mw	
		1335 mw	1328 w
			1347 w
1380 s	1374 w		1370 s
1400 sh	1396 w		1394 vw
1415 w	1411 s	1413s	
1450 sh	1451 m	1430 m	
1465 s		1480 s	
		1490 sh	1492 w
		1515 m	1514 mw
		1530 ms	1520 mw
1545 s	1556 m	1547 w	
1580 s			
			1619 m

Table III-7 (Contd.)

	1629 m, br		1624 m
1690 m		1660 s	
1725 w		1705 w	

- a) A. Girlando, B. Tamburini and C. Pecile, J. Chem. Soc. Faraday II, 1974, 70, 6.

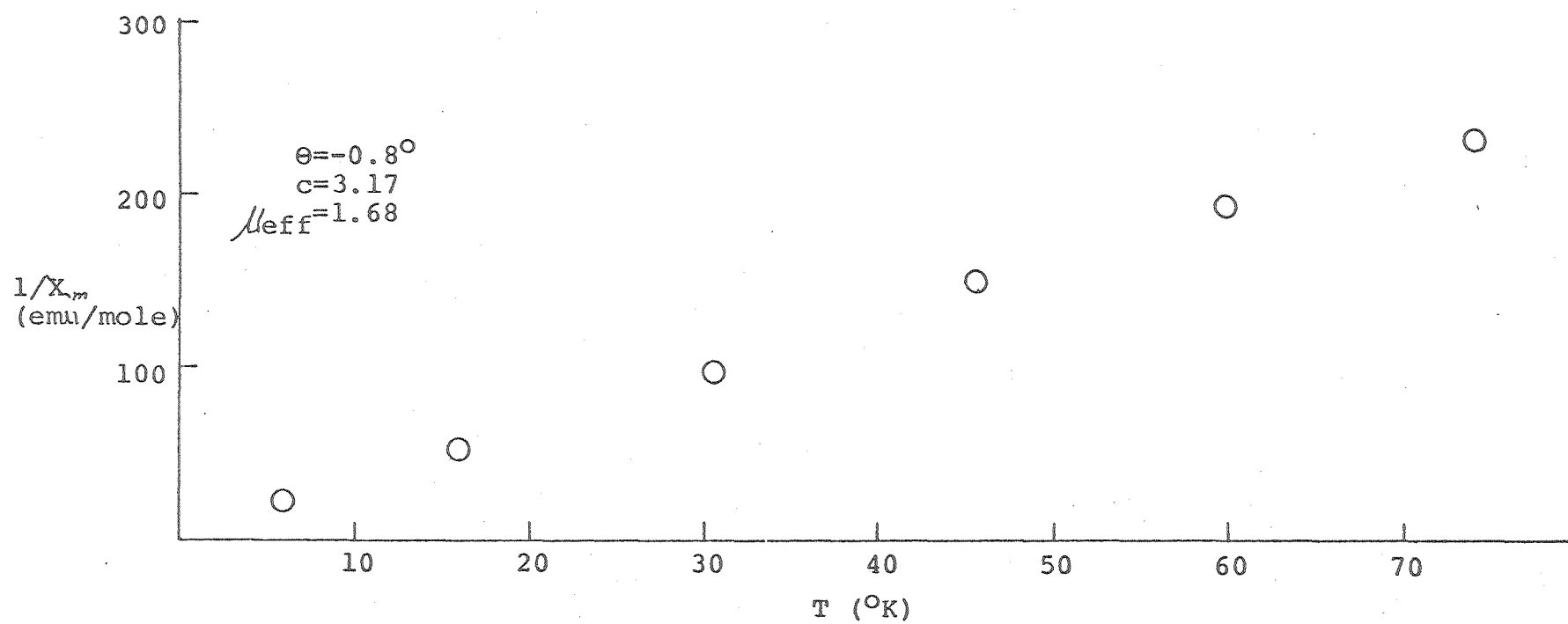


Figure III-1 Magnetic Susceptibility Data for $C_{10}F_8AsF_6$

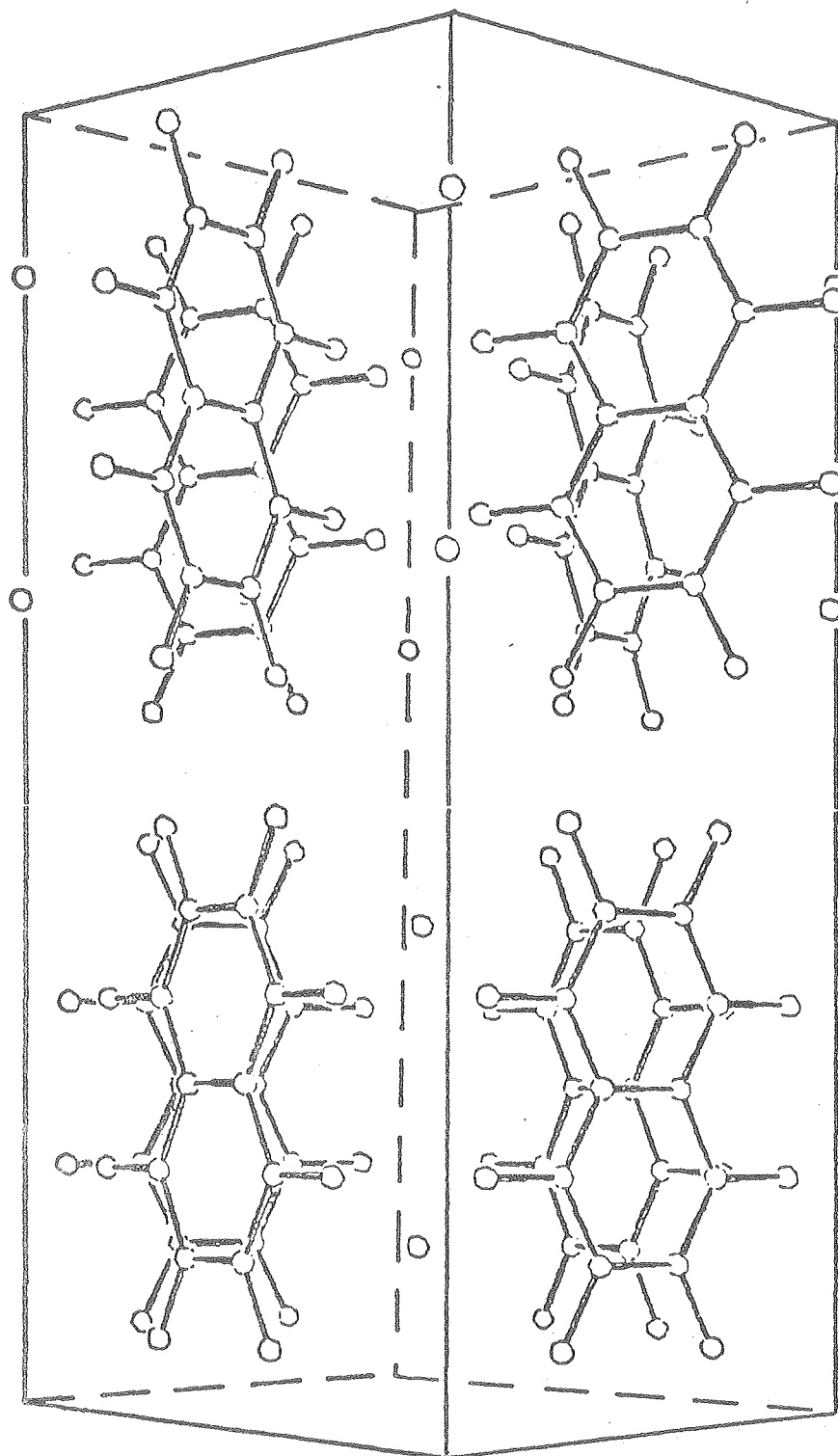


Figure III-2 Structure of $C_{10}F_8AsF_6$ (F atoms on As omitted)

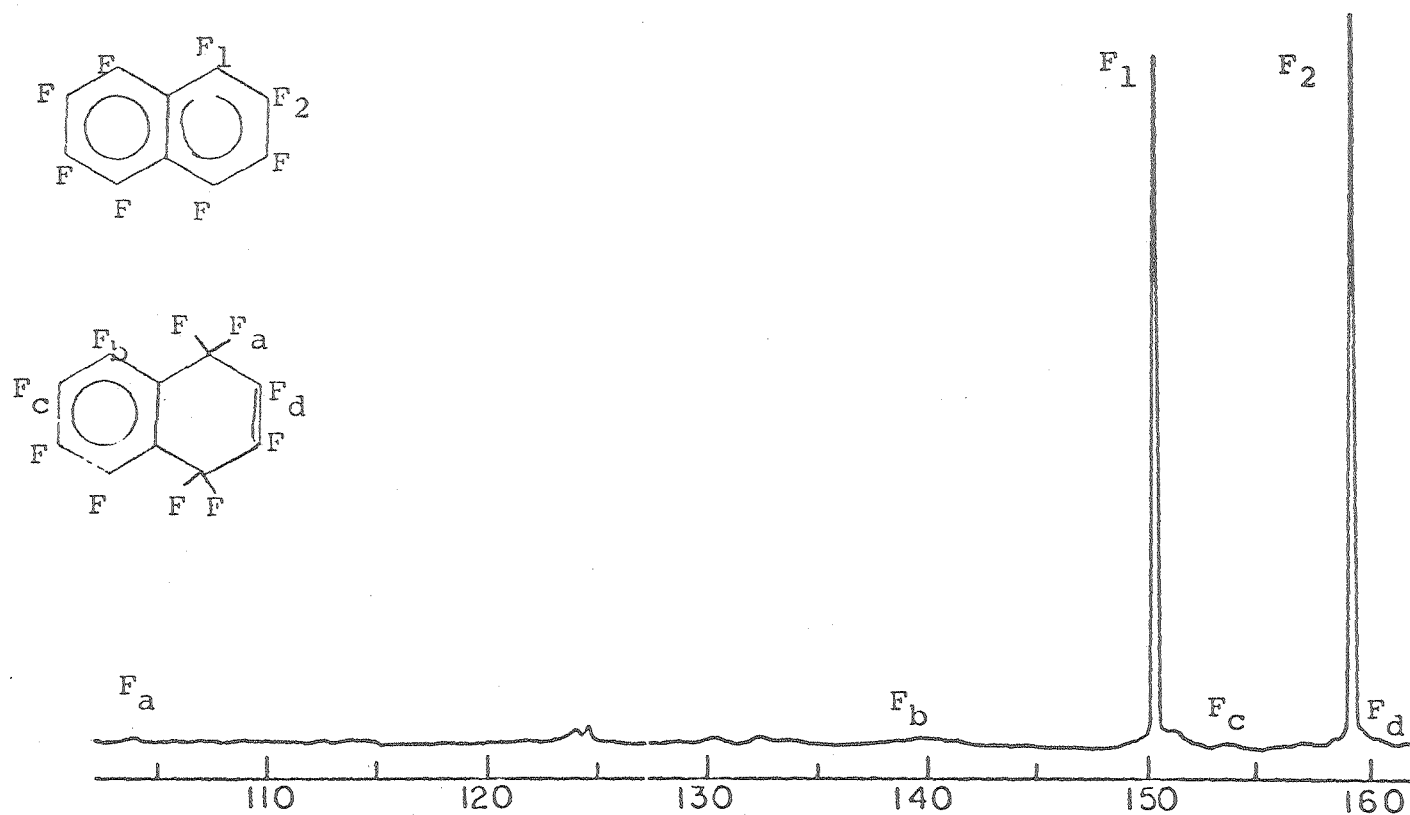


Figure III-3 ^{19}F NMR Spectrum of Products of Reaction: $\text{C}_{10}\text{F}_8\text{AsF}_6 + \text{CsF} \rightarrow$

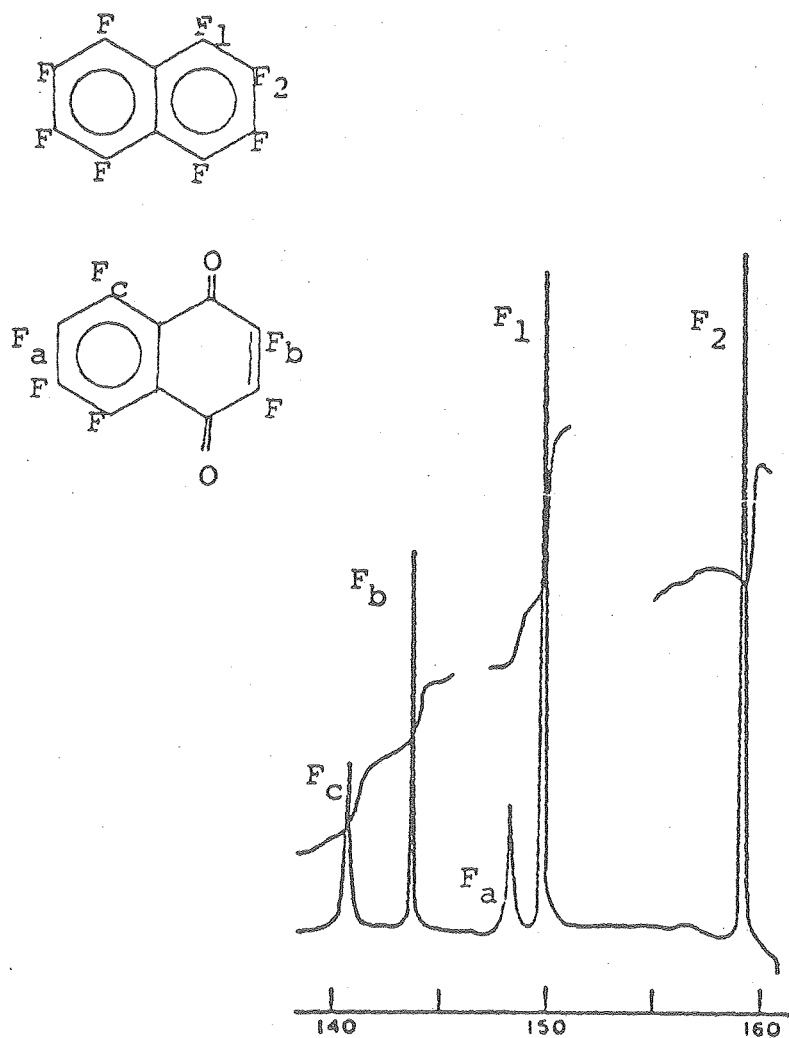


Figure III-4 ^{19}F NMR Spectrum of Hydrolysis Products of $\text{C}_{10}\text{F}_8\text{AsF}_6$

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5. C. Thompson and W. J. MacCulloch, Molecular Physics, 19, 817 (1970).
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IV. REACTION OF BENZENE WITH ARSENICPENTAFLUORIDE

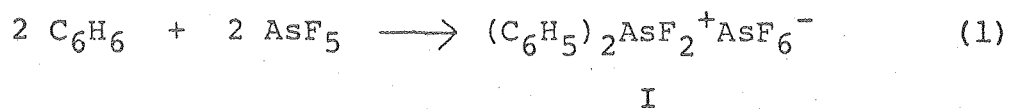
A. Introduction

The reaction of Benzene with $O_2^+AsF_6^-$ or $C_6F_6^+AsF_6^-$ gives a mixture of products (see Chapter V). In order to clarify that chemistry, the reaction of C_6H_6 with AsF_5 was undertaken on the assumption that the reactions with O_2AsF_6 and C_6F_6 generated some AsF_5 which could also interact with benzene.

No products have heretofore been reported for the reaction of C_6H_6 with either PF_5 , AsF_5 or SbF_5 , although $C_6H_5AsF_4$ and $C_6H_5PF_4$ have each been synthesized^{1,2} by other routes. When AsF_5 is passed into a solution of C_6H_6 in either HF or SO_2ClF a white crystalline product forms quickly and quantitatively. This is identical to one of the products from O_2^+ or $C_6F_6^+$ salt interactions with benzene. The physical and chemical evidence shows that it is the salt $(C_6H_5)_2AsF_2^+AsF_6^-$.

B. Results and Discussion

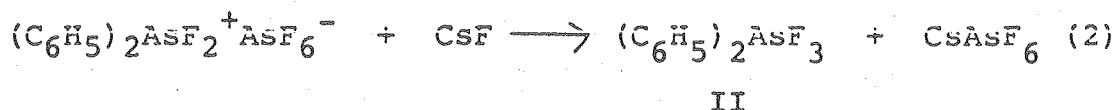
Benzene reacts with Arsenic pentafluoride to give the colorless, crystalline solid $(C_6H_5)_2AsF_2^+AsF_6^-$ (I) in quantitative yield:



I is a non-volatile solid that melts with decomposition at $\sim 150^\circ$ and the analytical data indicate an empirical

formula $C_6H_5AsF_4$. However, $\emptyset AsF_4$ is reported¹ to be a yellow liquid at ordinary temperatures. The ^{19}F NMR spectrum (in DMSO with $CFCl_3$ as reference) is given in Figure IV-1. The quartet at -61.7 ppm is characteristic³ of AsF_6^- and the singlet of one-third the intensity at -62.8 ppm suggests the cation $\emptyset_2AsF_2^+$. The shifts are independent of concentration. The mass spectrum obtained from the decomposition of I in the sample chamber of the mass spectrometer shows peaks at m/e corresponding to $\emptyset_2AsF_2^+$, \emptyset_2AsF^+ , $(C_6H_4)As^+$, $\emptyset AsF_2^+$ and AsF_2^+ . This evidence all indicates the formulation $(C_6H_5)_2AsF_2^+AsF_6^-$.

In order to characterize I chemically, the arsonium salt was reacted with CsF :



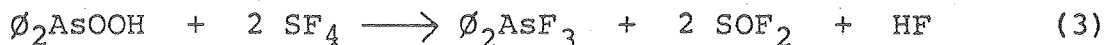
Reaction (2) gives II in quantitative yields. This has the same ^{19}F NMR spectrum (see Table IV-1) as that reported by Muetterties⁴ for \emptyset_2AsF_3 . The mass spectrum has (m/e) peaks corresponding to \emptyset_2AsF_3 , $\emptyset_2AsF_2^+$, \emptyset_2AsF^+ , $(C_6H_4)As^+$, $OAsF_3$, $\emptyset AsF_2^+$ and $\emptyset AsF^+$ as well as some smaller fragments. II is soluble in aromatic solvents and deliquesces quickly in moist air. Although these results are consistent with the formulation $(C_6H_5)_2AsF_3$, a small controversy in the literature prevented definite verification.

Littlefield and Doak⁵ questioned the published ^{19}F NMR spectrum. Muetterties had reported⁴ that the spectrum for

AsF_3 consisted of a doublet and triplet of relative intensity 2:1 with a common coupling constant of 67 Hz, suggesting a rigid trigonal bipyramid at room temperature.

Littlefield and Doak fluorinated AsH_3 or AsCl_3 with SF_4 to obtain a crystalline solid the ^{19}F NMR of which consisted of a singlet (at 69.1 ppm upfield of CFCl_3) relatively unchanged from -90° to room temperature. On the basis of elemental analyses this material was described as AsF_3 and the ^{19}F NMR findings were attributed to pseudo-rotation. In order to settle this controversy Muetterties' original preparation was repeated.

The reaction⁶:



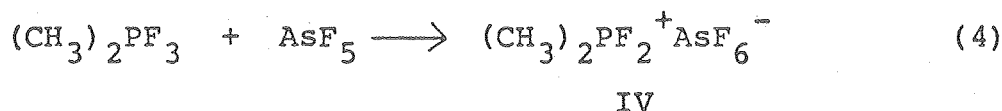
was run using a large excess of SF_4 in a Monel bomb. The crystalline product (approximately 40% yield) gave a mass spectrum identical to the one reported for II above. The ^{19}F NMR spectrum in toluene (see Table IV-1) consisted of a doublet and a triplet of relative intensity 2:1 with a coupling constant of 70 Hz. The spectrum showed no sign of coalescence in the temperature range -50° to 71° . This spectrum is identical with that of II. This leaves no doubt of the correctness of the original ^{19}F NMR studies of Muetterties and their interpretation. Evidently Littlefield and Doak did not have AsF_3 as they thought. Perhaps, because they derived their so-called $(\text{C}_6\text{H}_5)_2\text{AsF}_3$ from arsenic(III) species (AsH_3 or AsCl_3) they may not have

produced an arsenic(V) material.

To further the chemical characterization of $\emptyset_2\text{AsF}_3$, it was treated with AsF_5 and this resulted in an alternate synthesis of I:



Brownstein and Schmutzler⁸ have reported a similar reaction:



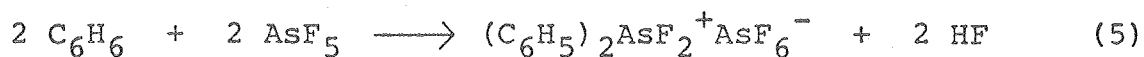
where IV was identified by its ^{19}F NMR spectrum but not isolated. These spectroscopic and chemical studies serve to fully characterize the reaction of benzene with AsF_5 .

Reactions (1) and (2) can be used as a quantitative route for the synthesis of $\emptyset_2\text{AsF}_3$ (100% yield based on benzene, 50% yield based on AsF_5). When compared to the 40% yield from the high pressure and temperature method of reaction (3) this new route seems to be a better general method for the clean synthesis of $\emptyset_2\text{AsF}_3$. In fact, other organic molecules may react with AsF_5 in a similar manner to give the synthesis of various types of R_2AsF_3 molecules. Furthermore it is possible that PF_5 and SbF_5 may also react in a similar manner to provide a method for the efficient syntheses of R_2PF_3 and R_2SbF_3 species. Therefore this route based on reactions (1) and (2) could possibly be a general method for the synthesis of pentasubstituted group V compounds of the type R_2MF_3 .

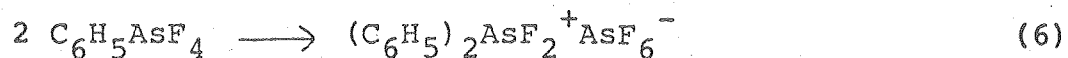
Having identified I as the crystalline component in the mixture resulting from the reaction of benzene with either O_2^+ or $C_6F_6^+$, the solubility of this salt in a variety of solvents was examined. It was found to be very soluble in anhydrous HF at room temperature.

Large needle-shaped crystallites were formed on cooling solutions to -78° . Although none were found which were suitable for a single crystal structure determination, a triclinic space group, consistent with the X-ray powder pattern, was determined by precession methods (see Table IV-2). The volume of the unit cell (326 \AA^3) is comparable to that estimated⁹ for $(C_6H_5)AsF_2^+AsF_6^-$ (320 \AA^3), which indicates one formula unit per unit cell.

Since $C_6H_5AsF_4$ is not observed in the product of the interaction of benzene with AsF_5 and since Smith¹ did not report I in the synthesis of $\emptyset AsF_4$, it seems unlikely that reaction (5) proceeds via a $\emptyset AsF_4$ intermediate:

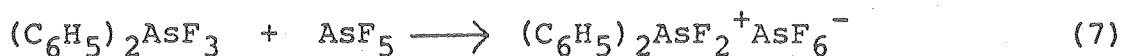


The possible disproportionation:



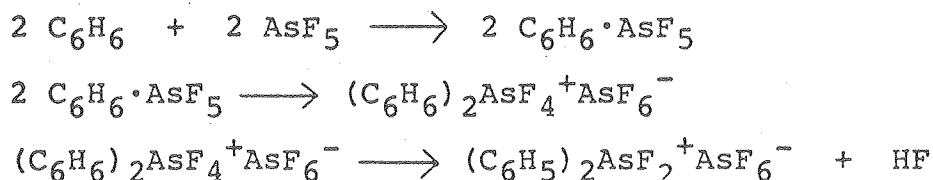
is not catalyzed by the presence of HF, since it is present in equimolar quantities as a by-product of Smith's synthesis of $\emptyset AsF_4$.

Another possible route for equation (5) is via \emptyset_2AsF_3 . Since \emptyset_2AsF_3 reacts with AsF_5 to give I:



and no $\text{C}_6\text{H}_5\text{AsF}_3$ was seen, even when a ten-fold excess of benzene was reacted with AsF_5 , reaction (7) is not considered a possible route for this reaction.

One possible mechanism for the production of I is through the formation of a $\text{C}_6\text{H}_6 \cdot \text{AsF}_5$ adduct followed by disproportionation.



The elimination of HF in the final step would irreversibly lead to products. It has been suggested from conductivity measurements¹⁰ that the $\text{CH}_3\text{CN} \cdot \text{AsF}_5$ adduct disproportionates to give $(\text{CH}_3\text{CN})_2\text{AsF}_4^+\text{AsF}_6^-$. HF elimination products from this cation have not been seen but the elimination of HF from such a cation may be less likely because of the protons of the CH_3 group being further from the F atoms of the AsF_5 entity than would be the case in a benzene/ AsF_5 adduct.

C. Experimental

1. Interaction of benzene with arsenic pentafluoride.

Arsenic pentafluoride (6.22 mmole, measured tensimetrically) was condensed into a Kel-F tube provided with a magnetic spinbar and subsequently SO_2ClF (5 ml) was condensed (from its purification vessel held at -45°). A molar excess of benzene was condensed onto the frozen solvent. With the

bottom half of the tube held at -78° the benzene in the upper half was allowed to melt at room temperature forming a green color upon solution. This was immediately followed by the formation of a copious colorless precipitate. To ensure completion of the reaction, the tube was held at 0° (with stirring) for one hour. Removal of solvent and drying under vacuum gave a white free-flowing crystalline solid, (0.41 g, 6.2 mmole).

Anal. Calcd for $C_6H_5AsF_4$: C, 31.60; H, 2.21; As, 32.9; F, 33.3%. Found: C, 31.77; H, 2.33; As, 33.1; F, 32.9%. The ^{19}F NMR spectrum (DMSO) is shown in Figure IV-1. IR: (Nujol Mull, cm^{-1}) 1575(w), 1342(w), 1272(w), 1185(w), 1078(w), 1065(m), 995(m), 742(s), 709(s), 675(s), 462(m), 398(m), 380(m). The mass spectrum of the volatiles from the solid at 125 showed the $C_{12}H_{10}AsF_2^{+}$ species to be the highest molecular weight fragment and of high abundance. X-ray powder and precession data are given in Table IV-1.

2. Interaction of $(C_6H_5)_2AsF_2^{+}AsF_6^{-}$ with CsF

$(C_6H_5)_2AsF_2^{+}AsF_6^{-}$ (0.46 g, 1 mmole) from above was mixed with cesium fluoride (0.15 g, 1 mmole) in a teflon tube. Anhydrous hydrogen fluoride (5 ml) was distilled onto the solids, and the mixture allowed to stand at room temperature for one hour, after which the solvent was removed under vacuum. The resultant white solid was transferred to a Teflon filtration apparatus and extracted with several batches of dry toluene. Removal of the toluene from the filtrate, under vacuum, gave a colorless solid (0.29 g,

1.0 mmole). The ^{19}F NMR spectrum (toluene) is given in Table IV-1.

Mass spectrum: m/e 286(4.2) $\text{C}_6\text{H}_5\text{AsF}_3^+$, 264(24.3) $\text{C}_6\text{H}_5\text{AsF}_2^+$, 248(5.0) $\text{C}_6\text{H}_5\text{AsF}^+$, 227(1.6) $(\text{C}_6\text{H}_5)_2\text{As}^+$, 209(11.0) $\text{C}_6\text{H}_5\text{AsF}_3^+$, 190(36.5) $\text{C}_6\text{H}_5\text{AsF}_2^+$, 171(14.8) $\text{C}_6\text{H}_5\text{AsF}^+$. The toluene-insoluble by product of the reaction was shown to be CsAsF_6 by its characteristic X-ray powder pattern

3. Interaction of $(\text{C}_6\text{H}_5)_2\text{AsF}_3$ with AsF_5

$(\text{C}_6\text{H}_5)_2\text{AsF}_3$ (0.210 g, 0.73 mmole), obtained as described above, was placed in a teflon tube and anhydrous hydrogen fluoride (5 ml) condensed on top of it. A molar excess of AsF_5 was condensed into the tube and the vessel was warmed to room temperature. The solid dissolved and the supply of AsF_5 was maintained until uptake ceased. The excess AsF_5 was removed under vacuum at -78° and the solvent at room temperature to give a colorless solid (0.331 g, 0.73 mmole). An X-ray powder pattern of this product was identical to that obtained from the benzene/ AsF_5 reaction.

4. Interaction of $(\text{C}_6\text{H}_5)_2\text{AsOOH}$ with SF_4

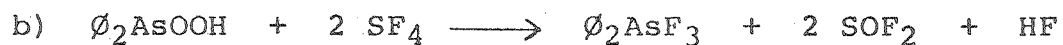
SF_4 (9.2 g, 85 mmoles) was condensed onto $(\text{C}_6\text{H}_5)_2\text{AsOOH}$ (4.4 g, 17 mmoles) in a Monel bomb. After being heated at 200° for 12 hours, the solid grey-colored product was placed in a 50 ml flask with 4 g of NaF. The product was dissolved in 20 ml petroleum ether, filtered and recrystallized to give colorless crystalline $(\text{C}_6\text{H}_5)_2\text{AsF}_3$ (2 g, 7 mmoles). The solid which melts with decomposition $\sim 135^\circ$, gives the same mass spectrum and ^{19}F NMR as described for

II above. The NMR was unchanged in the temperature range -50° to +71° (see Table IV-1).

Table IV-1 ^{19}F NMR of $(\text{C}_6\text{H}_5)_2\text{AsF}_3$



Shift ^a	Multiplicity ($J_{\text{F-F}}$)	Integration	Assignment
-69.8	doublet (71 Hz)	2	F _{axial}
-92.4	triplet (71 Hz)	1	F _{equatorial}



Shift ^a	Multiplicity ($J_{\text{F-F}}$)	Integration	Assignment
-70.0	doublet (72 Hz)	2	F _{axial}
-92.5	triplet (72 Hz)	1	F _{equatorial}

c) Variable Temperature NMR data for b)

Temperature	Shift ^a (F _{axial})	Shift ^a (F _{equatorial})	$J_{\text{F}_a-\text{F}_e}$ (Hz)
-50	-72.0	-91.8	72
0	-70.7	-92.4	72
31	-70.1	-92.6	72
40	-70.0	-92.6	70
50	-69.9	-92.6	69
61	-69.6	-92.8	59
71	-69.5	-92.8	48

a) Negative sign refers to ppm upfield of CFCl_3 .

Table IV-2 Powder Pattern of $\text{O}_2\text{AsF}_2^+\text{AsF}_6^-$ (Film No. 1402)

Triclinic: $a = 8.35(5)$, $b = 7.19(5)$, $c = 6.73(5)$ Å
 $\alpha = 73.85(5)$, $\beta = 69.99(5)$, $\gamma = 79.23(5)$
 $V = 326$ Å³, $z = 1$,

<u>hkl</u>	<u>d_{hkl}</u>	<u>104/d² (obs.)</u>	<u>104/d² (calc.)</u>	<u>Rel. Intensity</u>
	8.27	147		S
100	7.70	169	164	S
010	6.95	206	211	m
001	6.24	257	264	m
101	5.89	288	300	w
110	5.42	340	338	S
	5.04	394		w
$\bar{1}10$	4.81	432	413	ms
	4.60	473		w
	4.40	517		VW
$\bar{1}01$	4.28	546	557	ms
0 $\bar{1}1$	4.18	573	586	w
	4.07	605		w
	3.96	638		S
211	3.80	688	691	w
	3.71	726		w
	3.58	782		VW
210	3.48	819	792	m
020	3.40	863	846	w
112	3.32	907	919	m
120, $\bar{2}10$	325	944	935, 944	w
012	3.08	1052	1049	mw
$\bar{1}20$	3.02	1098	1086	w
$\bar{2}01$	2.93	1160	1177	w
$\bar{1}21$	2.81	1266	1259	w
$\bar{2}11$, 301	2.71	1360	1355, 1357	m



Shift	Multiplicity	Integration	Assignment
-61.7	equal intensity quartet (930Hz)	3	AsF_6^-
-62.8	singlet	1	O_2AsF_2^+

Figure IV-1 ^{19}F NMR Spectrum of $(\text{C}_6\text{H}_5)_2\text{AsF}_2^+\text{AsF}_6^-$

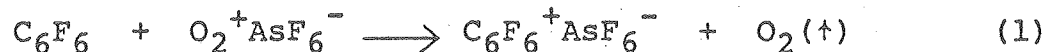
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V. ELECTRON OXIDATION OF BENZENE

A. Introduction

The radical cation of benzene has been characterized as a gaseous and as a matrix isolated species but salts are unknown. As ESR spectrum has been reported¹ for $C_6H_6^+$ obtained from UV irradiation of benzene in a rigid glassy matrix. More recently the cation has been identified and characterized in photoionization,² atom and ion bombardment,³ ion-cyclotron resonance,⁴ and chemical ionization mass spectrometry⁵ studies. It has not been produced⁶ however, in solution by chemical oxidation, nor have stable salts been formed. The salt of the perfluoro-relative, $C_6F_6^+AsF_6^-$, has been prepared and structurally characterized by Bartlett and Richardson:⁷



Although $C_6F_6^+AsF_6^-$ is not thermally stable at room temperature, decomposition is slow enough to have permitted its physical and chemical characterization at ordinary temperatures. It was recognized that a $C_6H_6^+AsF_6^-$ salt was likely to decompose by deprotonation as a consequence of HF elimination but it was hoped that the salt could be formed and preserved at temperatures well below room temperature.

In addition to $O_2^+AsF_6^-$, $C_6F_6^+AsF_6^-$ was perceived to be strongly oxidizing enough to oxidize benzene. Indeed the higher solubility of the latter in solvents such as anhydrous hydrogen fluoride and sulfuryl chloride fluoride as well as

as its clean decomposition at ordinary temperatures (see Chapter III) make it the oxidant of choice. The reaction of benzene with either of these salts yielded a mixture containing $(C_6H_5)_2AsF_2^+AsF_6^-$ and a dark-brown polymeric solid. The former compound and its quantitative synthesis from benzene and AsF_5 has been described in the previous chapter. In this chapter the isolation and characterization of the polymer is described.

B. Results and Discussion

The mixture derived from the oxidation of benzene by either O_2AsF_6 or $C_6F_6AsF_6$ was triturated with anhydrous HF in a Teflon filtration system to dissolve the diphenyl difluoroarsonium salt, $(C_6H_5)_2AsF_2AsF_6$. The polymeric residue amounted to 20-30% by weight of the product depending on the preparation. The polymer, which was amorphous to X-rays, proved to be insoluble in HF, DMSO, C_6H_6 , SO_2 , SO_2ClF and $(CF_3)_2CO$. All samples of the polymer fluoresced strongly in the laser beams, hence Raman spectra were not obtained. The IR spectrum (see Figure V-1), however, shows a close correspondence to that reported⁸ for poly (p-phenylene) with the addition of two bands at 700 and 395 cm^{-1} . The last can be assigned with confidence to ν_3 and ν_4 respectively of the AsF_6^- ion.⁹

The elemental analyses of the polymeric product from various preparations are given in Table V-1. These are consistent with the general formula $(C_6H_4)_xAsF_6$, where the value of x ranges from 1.8 to 4.4, depending upon the

preparation. The analytical difficulties probably stem from the difficulty in analyzing for fluorine in hexafluoroarsenates and vice versa. The telling feature of the analyses is that the C/H ratio is close to 6:4 for all samples. This, together with the infrared data, argues for an AsF_6^- salt of electron-oxidized poly(p-phenylene).

Baughman and coworkers have recently reported¹⁰ that pure poly(p-phenylene) reacts with AsF_5 to give a doped polymer. However, as with graphite, it is likely that the guest species is not AsF_5 but AsF_6^- with the AsF_5 oxidizing according to the equation:

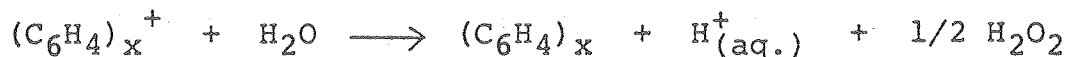


It is unclear how AsF_3 could be incorporated into the polymer and it seems likely that it is simply a volatile product. The IR spectrum of the polymer shows no bands attributable to molecular AsF_3 or AsF_5 . Thus the doped polymer prepared by Baughman et al may be very similar to the polyphenylene salt prepared in this work.

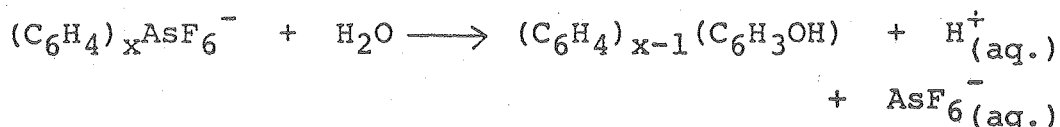
Using conventional 4-point probe methods Baughman reported a conductivity of $1\text{-}460 \text{ ohm}^{-1}\text{cm}^{-1}$ for a pressed powder of AsF_5 -doped polymer. Crude resistivity measurements (see Chapter II) on the polyphenylene salt set $0.01 \text{ ohm}^{-1}\text{cm}^{-1}$ as the lower limit of its conductivity. It is probable that the conductivity of a monolithic sample would be much higher.

When the polyphenylene salt is treated with water at

room temperature its color and texture do not visibly change. The product, however, has a greatly increased C and H content ($C + H\% > 70\%$), but the ratio of C to H remains 6:4. It is probable that the polyphenylene salt is simply oxidizing the water and that the product is a mixture of polyphenylene and solid hydrolysis products. No gas evolution was noted during the reaction but peroxide could have been an oxidation product:



It is possible, however, that the hydrolysis of the polyphenylene salt could result in the production of hydroxylated material according to the equation:

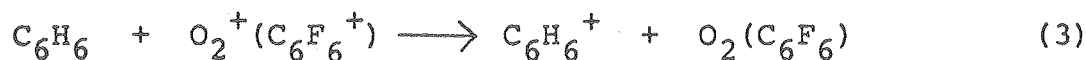


When $(C_6H_4)_{3.3}AsF_6$ is treated with a sodium dispersion in toluene the C and H content increases and the ratio of C to H falls to 1:1. The reaction is analagous to the Birch reduction of substituted benzenes to give substituted cyclohexadienes. The product expected from polyphenylene would be the cyclohexadiene polymer $\{C_6H_6\}_n$.

The analytical and spectroscopic information and the chemical and physical behavior of the polymeric materials are all consistent with its formulation as a poly(p-phenylene) hexafluoroarsenate salt. Curiously none of this polymeric material is formed in the interaction of benzene

with AsF_5 . This is relevant to the discussion of the mechanism of the reactions forming the polyphenylene salt.

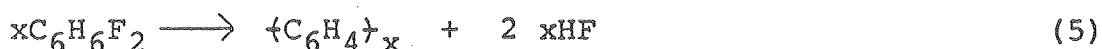
It seems likely that the first step in the reaction of benzene with C_6F_6^+ or O_2^+ involves electron transfer to form C_6H_6^+ :



Although the C_6H_6^+ ion can be maintained in a matrix¹ at -150° , spectroscopic studies⁶ have shown that it is difficult to stabilize at ordinary temperatures. The room temperature decomposition could proceed in a manner similar to the pyrolysis of $\text{C}_6\text{F}_6\text{AsF}_6$ (see Chapter III) to give an analogous cyclohexadiene along with benzene:

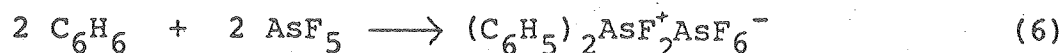


HF elimination from $\text{C}_6\text{H}_6\text{F}_2$ would generate polyphenylene:



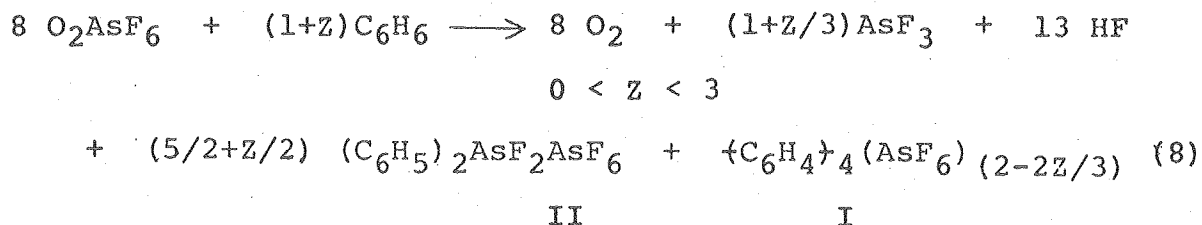
The polyphenylene isomer formed in (5) would depend on which isomer of $\text{C}_6\text{H}_6\text{F}_2$ were formed in (4).

The mechanism concludes with the benzene and polyphenylene competing for the limiting quantity of AsF_5 according to the following steps:



Reaction (6) is discussed in Chapter IV and (7) is a plausible interpretation for the findings¹⁰ of Baughman et al.

The reaction of O_2AsF_6 with an excess of C_6H_6 roughly obeys the following reaction stoichiometry:



Z , which determines the ratio of the polyphenylene salt to the arsonium salt formed, will depend on the relative rates of the proposed reactions (6) and (7).

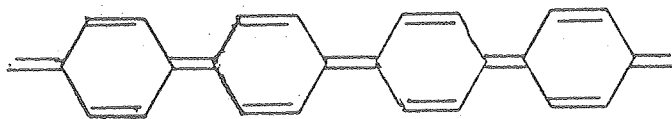
The variability of the composition of the salt $(\text{C}_6\text{H}_4)_x^- \text{AsF}_6$ is, of course, attributable to the competition of these two latter reactions. The ratio of the masses $\text{I}/(\text{I}+\text{II})$, the carbon content of I, and the ratio of the masses $(\text{I}+\text{II})/-\text{O}_2\text{AsF}_6$ are listed for the products of four preparations in Table V-2. Calculated values for these quantities, based on appropriate values of z (see footnote in Table), are also listed.

The ratios (mmoles C_6H_4 formed/mmoles O_2AsF_6 used) for each reaction are also given in Table V-2. The mechanism under consideration requires one mole of C_6H_4 to be formed for every two moles of O_2AsF_6 expended.

The reactions represented by entires 1 and 4 were allowed

to proceed very quickly. This probably resulted in local heating and hence decomposition of O_2AsF_6 to give AsF_5 which reacted with benzene to give $(C_6H_5)_2AsF_2^+AsF_6^-$. In turn the amount of $C_6H_6^+AsF_6^-$ formed decreases, causing large deviations from the calculated mass ratios and carbon content. The preparations represented by entries 2 and 3, however, proceeded very slowly and provide better agreement with the calculated values. These findings are consistent with the proposed mechanism giving (8) as the net reaction.

The moderate electrical conductivity of the polyphenylene salt contrasts sharply with the insulator properties of pure poly(p-phenylene). This is consistent with the production of electron hole carriers in the valence band of the poly(p-phenylene). This band can be identified with the π -orbital system of the polymer and the conductivity suggests that there may be appreciable contribution from the planar conjugated form:



which would permit electronic interaction between the rings. Because the close approach of the hydrogen atoms on adjacent rings acts as a steric hindrance to planarity, it is generally accepted that this form does not play an important role in the bonding of pure poly(p-phenylene) which is consistent with its nature as an insulator.

c. Experimental

1. Interaction of Benzene with $O_2^+AsF_6^-$

SO_2ClF (5 ml) was condensed into a passivated teflon tube containing $O_2^+AsF_6^-$ (0.912 g; 4.13 mmoles). Benzene (0.403 g, 5.16 mmole) and more SO_2ClF (3 ml) were condensed onto the frozen mixture. A green-colored solution resulted as the reaction was warmed to -78° . When gas evolution ceased (15 minutes), all volatiles were removed under vacuum at room temperature yielding a dark-brown-colored solid (0.893 g). The residue was triturated several times with anhydrous hydrogen fluoride to give, after filtration, a brown powder (0.182 g). See Table V-1 (preparation No. 1) for analytical details. The IR spectrum is presented in Figure V-1. Removal of solvent from the filtrate under vacuum yielded a colorless solid shown to be $(C_6H_5)_2AsF_2^+-AsF_6^-$ by its characteristic X-ray powder pattern.

2. Interaction of Benzene with $C_6F_6^+AsF_6^-$

O_2AsF_6 (0.473 g, 2.14 mmoles) was reacted with an excess of hexafluorobenzene in SO_2ClF as described in Chapter III. After gas evolution stopped, the volatiles were removed at -78° and benzene (0.323 g, 4.14 mmole) was condensed onto the reaction mixture. The mixture was allowed to stand at -78° for one hour and all volatiles were subsequently removed at room temperature. The brown-colored solid (0.546 g) was triturated with anhydrous hydrogen fluoride as above to yield a brown powder (0.134 g). Anal. Calcd for $(C_6H_4)_{3.6}AsF_6$: C, 56.03; H, 3.11; As, 16.21;

F, 24.64%. Found: C, 55.85; H, 2.87; As, 13.62; F, 16.99%.

The IR spectrum was essentially the same as that seen for the C_6H_6/O_2AsF_6 reaction product. $(C_6H_5)_2AsF_2AsF_6$ was isolated from the filtrate as described above.

3. Reaction of $(C_6H_4)_3.3AsF_6$ with H_2O

A small sample of $(C_6H_4)_3.3AsF_6$ formed from the $C_6H_6/C_6F_6^+AsF_6$ reaction described above was stirred with 10 ml of distilled water for 2 hours and collected on a glass frit. After several washing, subsequent air-drying for eight hour yielded a brown powder. Anal. Calcd for $(C_6H_4)_{12.7}(C_6H_3OH)(AsF_6)_2$: C, 68.73; H, 3.81%; C/H ratio, 1.50. Found: C, 68.82; H, 3.79%; C/H ratio, 1.51.

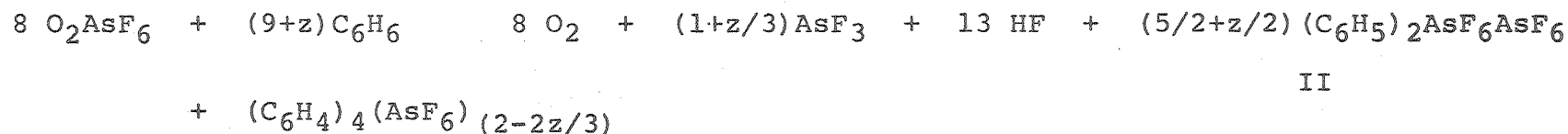
4. Reaction of I with Sodium Slurry

A small sample of $(C_6H_4)_3.3AsF_6$ was reacted with sodium lumps in refluxing toluene for 30 minutes. After cooling, the excess Na was destroyed with 95% ethanol and the product filtered with a glass frit. After washing with 500 ml of distilled water, subsequent air-drying for eight hours yielded a brown powder. Anal. Calcd for $(C_6H_6)_5AsF_6$: C, 62.17; H, 5.18%, C/H ratio, 1.0. Found: C, 61.90; H, 5.45%; C/H ratio, 0.95.

Table V-1 Analytical Data on $(C_6H_4)_xAsF_6$ Obtained from Various Preparations

Preparation No.	C	H	As	F	C/H ratio	Comments
1	54.11%	2.79%	14.68%	18.76%	6:3.7	
1	53.94	2.72	13.83	22.07	6:3.6	from O_2AsF_6
2	55.85	2.87	13.62	16.99	6:3.7	from $C_6F_6AsF_6$
3	46.56	2.58		28.27	6:40	from O_2AsF_6 , F analysis by K-Fusion
4	54.85	3.32			6:4.4	from O_2AsF_6
5	60.34	3.44			6:4.0	from O_2AsF_6
6	44.4	2.30			6:3.7	from O_2AsF_6
7	39.20	2.16			6:40	from O_2AsF_6

Table V-2 Experimental Mass Ratios and Analytical Data from the Reaction of C_6H_6 with $O_2AsF_6(C_6F_6AsF_6)$ Compared with those Computed on the Basis of Equation 8



I

II

Preparation ^a Number	z ^b	wt. I		% C in I		wt. I + wt. II		mmoles of pri- mary oxidant mmoles of C_6H_4 in I
		wt. I	wt. I + wt. II	found	calculated	wt. O_2AsF_6	calculated	
1	1.5	0.25		41.9	58.4	0.60	1.12	4.7
2	1.9	0.22		60.3	65.1	1.06	1.14	2.3
3	1.5	0.25		55.9	58.4	1.15	1.12	2.1
4	2.2	0.20		54.1	71.1	0.98	1.16	3.0

- a) Because of local heating, entries land 4 are less dependable than 2 and 3.
- b) Selected so as to make the calculated ratio for wt. I/(wt. I + wt. II) equal the observed ratio.

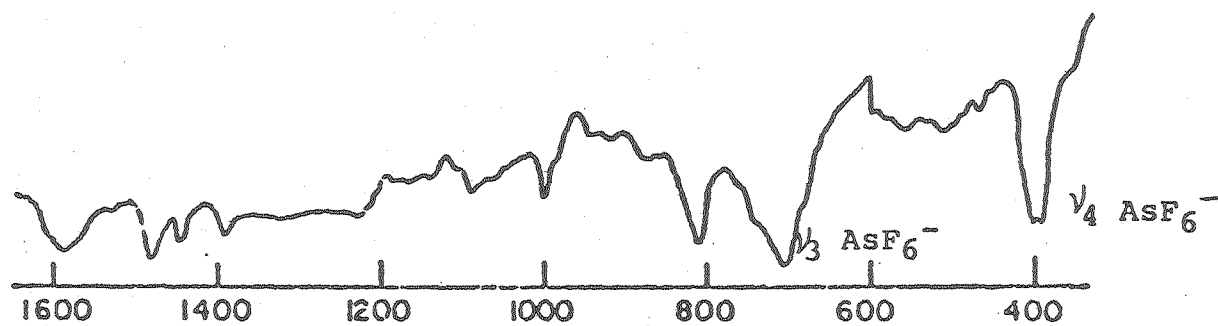


Figure V-1. IR Spectrum of $(\text{C}_6\text{H}_4)_{3.3}\text{AsF}_6$

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VI. ELECTRON OXIDATION OF NAPHTHALENE, ANTHRACENE AND CORONENE

A. Introduction

Lewis and Singer¹ obtained ESR spectra from solutions of various poly-aromatics with SbCl_5 . The spectra obtained from a solution of naphthalene was assigned to the dimer radical cation $(\text{C}_{10}\text{H}_8)_2^+$. Fritz and coworkers² reported the crystal structure of $(\text{C}_{10}\text{H}_8)_2\text{PF}_6$ synthesized electrochemically from a solution of naphthalene and PF_5 . No resolved ESR spectra have been reported for any cations derived from anthracene. The coronene radical mono-positive cation has been observed³ in superacid solution.

This project was undertaken to synthesize radical cation salts of naphthalene, anthracene and coronene. Because such cations would be larger, in at least one dimension, it was thought that close packing of anions and cations would enforce cation-cation overlap (Figure VI-1). Such overlap ought to bring the π clouds of the cations into an overlapping situation and, therefore, facilitate such delocalization. Since the large aromatic molecules have low ionization potentials it seemed likely that the salts would be thermally stable. The large number of multi-ring aromatics available provides for the synthesis of an even larger range of salts since a variety of anions (including species such as $\text{Sb}_2\text{F}_{11}^-$ and $\text{Sb}_3\text{F}_{16}^-$) can also be employed. Thus there is here the potential here for a range of conductors some of which could be semiconductors and others good metals.

Since the oxidative intercalation^{4,5} of graphite with AsF_5 or MF_6 ($\text{M} = \text{Ir}, \text{Os}$ or Pt) can form the highly oxidized materials $\text{C}_8^+\text{MF}_6^-$ and $\text{C}_{12}^{2+}\text{MF}_6^{2-}$ (the C_8MF_6 stoichiometry being a consequence of a close packing unit) multiply-charged cations of these larger polyaromatics seemed feasible when extraordinarily strong oxidizing agents are used. O_2AsF_6 and $\text{C}_6\text{F}_6\text{AsF}_6$ were used principally in the oxidation of these polyaromatics although the high electron affinity of AsF_5 in the half-reaction (estimated to be 135 kcal/mole of electrons):



has also been exploited.

Naphthalene, phenanthrene, anthracene and coronene have each been oxidized but the emphasis has been on the last. A major experimental difficulty has been associated with the failure to find a suitable solvent for the development of monolithic samples. X-ray powder patterns and elemental analyses have been used to characterize the products. To probe for evidence of electron delocalization, the powdered products, when obtained pure, were subjected to crude resistivity measurements. Magnetic susceptibility measurements were also carried out to investigate the possibility of cation-cation interactions.

2. Results and Discussion

Since experimental difficulties prevented the confident characterization of the coronene oxidation products,

one or more rationalizations, consistent with the data obtained, has been suggested for each of the three reactions studied. These reactions are: the interaction of coronene with 1) a large excess of O_2AsF_6 , 2) an equimolar quantity of O_2AsF_6 and 3) a large excess of $\text{C}_6\text{F}_6\text{AsF}_6$. Each gave a different product from the others.

When coronene is reacted with a large excess of O_2AsF_6 a dark-green colored product which analyses as $\text{C}_{24}\text{H}_{12}(\text{AsF}_6)_2$ is formed:



When a very large excess of oxidant is used and the reaction is allowed to proceed very slowly the product formed analyses as $\text{C}_{24}\text{H}_{12}(\text{AsF}_6)_2.0$. Since the IR spectrum (Figure VI-2) is similar to that for coronene with the addition of ν_3 and ν_4 of AsF_6^- at 700 and 390 cm^{-1} , it seems likely that the product is a salt of the coronene dication. However other physical data does not support this formulation.

Two preparations of $\text{C}_{24}\text{H}_{12}(\text{AsF}_6)_2$ obtained similarly gave different X-ray powder patterns. This together with the poor quality and low intensity of the patterns suggests that the material is a mixture of an amorphous major component and a microcrystalline minor component. If each of these two product mixtures have a different minor component this would account for the different X-ray powder patterns. The magnetic susceptibility data on one sample of $\text{C}_{24}\text{H}_{12}^-(\text{AsF}_6)_2$ (Figure VI-3) obeys the Curie-Weiss law with $\theta = 5.9^\circ$

and $C = 0.075$ but the magnetic moment is low ($\mu_{\text{eff}} = 0.83$). This can be accounted for by a mixture composed of one diamagnetic component and a magnetically dilute component.

Crude resistivity measurements on $\text{C}_{24}\text{H}_{12}(\text{AsF}_6)_2$ show that $\rho < 10^4$ ohm \cdot cm; which indicates that the product exhibits a large amount of electron delocalization (since coronene itself is an insulator). The paramagnetic compound is unlikely to be the electron-delocalized material particularly since the small value of the Weiss constant indicates a magnetically dilute system. The paramagnet is presumably the minor component. It is possible that the conductor is a $(\text{C}_{24}\text{H}_{10}(\text{AsF}_6)_2)_x$ salt involving polymerization of the coronene and akin to the polyphenylene salt of Chapter V. This product may have a two-dimensional layered structure similar to that of graphite, although a sheet structure is not the sole possibility. Since the polyphenylene salt is a diamagnetic, amorphous material, the polymeric coronene salt should make up the diamagnetic, amorphous component of the mixture. There is, however, no direct evidence for the formation of any polymeric material in the oxidation of coronene.

The microcrystalline material could be a paramagnetic simple coronene salt or a salt of a decomposition product of a coronene cation. Since the powder patterns from samples of similar composition are unrelated there are clearly several distinct minor components.

In some reactions of coronene with excess O_2AsF_6 where the reaction was allowed to proceed rapidly, the products

formed analyzed as $C_{24}H_{12}(AsF_6)_x$ where x ranged from 1.4 to 1.9. These samples exhibited properties similar to $C_{24}H_{12}(AsF_6)_2$. When coronene was reacted with excess $C_6F_6AsF_6$:



the products formed exhibiting properties similar to those described above for $C_{24}H_{12}(AsF_6)_2$. No magnetic susceptibility data was obtained on these latter products.

The reaction of coronene with an equimolar amount of O_2AsF_6 :

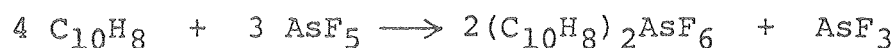


gave a dark-green product which analyzed as $C_{24}H_{12}(AsF_6)_{1.1}$. The IR spectrum (Figure VI-4) is not distinguishable from that of $C_{24}H_{12}(AsF_6)_2$. The amorphous product exhibited a very low magnetic moment ($\mu_{eff} = 0.25$). The magnetic susceptibility data (given in Figure VI-5) obeys the Curie-Weiss law with $\theta = -1.8^\circ$ and $C = 0.016$. Again, this suggests the presence of a small amount of paramagnetic impurity. The electrical conductivity ($\rho < 5 \times 10^3 \text{ ohm}\cdot\text{cm}$) could arise from a delocalized electron salt of a polymeric coronene derivative as has been suggested above for $C_{24}H_{12}(AsF_6)_2$.

The anticipated π -cloud overlap of cationic species could be occurring but it appears to be more likely that a more extended polymeric cation salt is being formed. However, at this point, the distinction between the two models

becomes a semantic one. Significant progress in these studies will depend upon the discovery of a superior solvent or a very slow and controlled synthesis to form crystalline material.

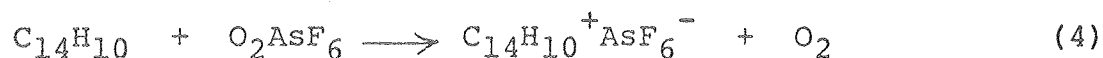
Although no conclusive evidence has been gathered, the oxidation of naphthalene, anthracene and phenanthrene do form products analagous to those seen from coronene. Naphthalene reacts with AsF_5 to give a dark purple solid, the probable reaction being:



III

III is the product expected by analogy to the electrochemical synthesis of $(\text{C}_{10}\text{H}_8)_2\text{PF}_6$ by Fritz et al.² The elemental analyses indicate that some charring occurred during reaction (3) giving a graphitic byproduct along with III. The lack of crystallinity in the solid prevented further chatacterization.

Anthracene reacts with O_2AsF_6 to give a dark purple solid, the probable reaction being:



IV

Since both the monomer and dimer cations of anthracene have been observed in solution⁶, and the ionization potential of anthracene (7.6 eV) is much less than that of C_6F_6 (9.97 eV), IV is the expected product from the reaction of anthracene

with O_2AsF_6 . The low yield (17%) is probably due to decomposition of some O_2AsF_6 from local heating, unreacted anthracene being pumped away. The powder pattern (Table VI-1) contains few high-angle reflections and was not indexed.

The interaction of phenanthrene with O_2AsF_6 resulted in coloration of the surfaces of the phenanthrene crystals but the bulk of the phenanthrene did not react. The very low solubility of both reactants and product prevented any appreciable reaction from taking place.

Clearly the inability to find a solvent compatible with both the polyaromatic solids and the strong oxidizing agents has hampered this research. A solvent that permits a low-temperature heterogeneous oxidation reaction would be ideal for the study of these aromatic cation salts. CH_2Cl_2 , which dissolves the aromatics (except coronene) at -25° , should be excellent for reaction with $\text{C}_6\text{F}_6^+\text{AsF}_6^-$. Since the ionization potential of NO (9.25 eV) is greater than that of the aromatics (7.1 \rightarrow 8.1 eV) $\text{NO}^+\text{AsF}_6^-$ or NO^+BF_4^- (which are soluble in CH_2Cl_2) could provide for oxidation of naphthalene, anthracene, and phenanthrene.

These preliminary studies show that cation salts of naphthalene, anthracene and coronene may be synthesized by electron oxidation but single crystal samples are essential to meaningful physical studies.

C. Experimental

1. Interaction of Naphthalene with AsF_5

Naphthalene (0.2 g) was dissolved in dry C_6F_6 (5 ml) in one arm of a teflon filtration apparatus. AsF_5 (1 atm)

was maintained above the solution until uptake ceased. Large amounts of purple solid precipitated. After the AsF_5 was removed under vacuum, the precipitate was filtered off and pumped to dryness. The fluffy purple-colored powder proved to be amorphous to X-rays. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{AsF}_6$: C, 53.93; H, 3.95%; C/H ratio, 1.25. Calcd for $\text{C}_{30}\text{H}_{24}\text{AsF}_6$: C, 62.83; H, 4.19%; C/H ratio, 1.25. Found: C, 59.78; H, 2.81%; C/H ratio, 1.77. Attempts to record IR and Raman spectra failed.

2. Interaction of Anthracene with O_2AsF_6

O_2AsF_6 (0.49 g, 2.2 mmoles) and anthracene (0.49 g, 2.2 mmoles) were placed in a Kel-F tube and were separated by a teflon filter paper. After 5 ml of WF_6 was condensed into the tube and warmed to 0° large amounts of green solid were formed. After one hour the solvent was removed under vacuum to yield 0.14 g of dark-green product. The X-ray powder data are listed in Table VI-1. Attempts to record IR and Raman Spectra failed.

3. Interaction of Phenanthrene with O_2AsF_6

O_2AsF_6 (0.61 g, 2.8 mmoles) was reacted with phenanthrene (0.25 g, 1.4 mmoles) as described for anthracene to give 0.30 g of dark-green product. The product was phenanthrene coated with a thin layer of nearly black product. The X-ray powder pattern showed only the lines of phenanthrene.

4. Interaction of Coronene with excess $\text{C}_6\text{F}_6^+\text{AsF}_6^-$

O_2AsF_6 (1 g, 4.5 mmoles) was reacted with excess

C_6F_6 in SO_2ClF at -78° to give complete conversion to $C_6F_6AsF_6$. After the O_2 was removed at -196° , coronene (0.150 g, 0.500 mmol) was added to the tube, which was cooled to -196° in the dry N_2 atmosphere of a glove bag. After the N_2 was removed at -196° , large amounts of dark-green solid were formed at -78° . After 90 minutes the solvent was removed to give a free flowing dark-green solid. Anal. Calcd for $C_{24}H_{12}As_2F_{12}$: C, 42.50; H, 1.78%. Found: C, 41.25; H, 2.04%. All attempts to obtain IR and Raman spectra failed. The X-ray powder pattern bore no resemblance to those from any other oxidation product the intensity of the reflections diminished sharply at high angles.

In another preparation, coronene (0.10 g, 0.33 mmol) was reacted with excess $C_6F_6AsF_6$ in a similar manner to give a dark-green product. Anal. Calcd for $C_{24}H_{12}As_2F_{12}$: C, 42.50; H, 1.78%. Found: C, 43.24; H, 1.90%. Again no IR spectra could be obtained and the powder pattern, which contained no discernible high-angle reflections, had no reflections in common with the pattern obtained above or with any other powder pattern obtained from coronene oxidation products.

5. Interaction of Coronene with excess O_2AsF_6

O_2AsF_6 (1.25 g, 5.7 mmol) was placed in a tube with coronene (0.346 g, 1.15 mmol) as described above for anthracene. The reaction proceeded at -78° after addition of SO_2ClF (5 ml). The excess O_2AsF_6 was destroyed with C_6F_6 before removing all volatiles under vacuum to give a green free-flowing solid. Anal. Calcd for $C_{24}H_{12}As_2F_{12}$: C, 42.50;

H, 1.78%. Found: C, 42.59; H, 1.80%. The IR spectrum (KBr pellet) is shown in Figure VI-2. The X-ray powder pattern contained no discernible high-angle reflections nor did it resemble any of the powder patterns obtained from other coronene oxidation products. Magnetic susceptibility data are presented in Figure VI-2.

In another preparation, coronene (0.100 g, 0.33 mmoles) was reacted with O_2AsF_6 (0.500 g, 2.25 mmoles) in a similar manner to that described above to give a dark-green powder. Anal. Calcd for $C_{24}H_{12}As_2F_{12}$: C, 42.50; H, 1.78%. Found: C, 42.86; H, 1.83%. The IR spectrum is essentially the same as that recorded from the above product. The X-ray powder pattern contained no discernible high-angle reflections and bears no resemblance to the above or any other powder pattern recorded from coronene oxidation products.

In another preparation, coronene (0.100 g, 0.33 mmole) was reacted with O_2AsF_6 (0.145 g, 0.66 mmole) in a manner similar to that described above except no C_6F_6 was used. This yielded a dark-green colored powder. Anal. Calcd for $C_{24}H_{12}As_2F_{12}$: 42.50; H, 1.78%. Found: C, 46.53; H, 2.08%. All attempts to obtain an IR or Raman spectrum failed. The X-ray powder pattern showed no resemblance to any of the other patterns obtained from coronene oxidation products.

6. Interaction of Coronene with an Equimolar Amount of O_2AsF_6

O_2AsF_6 (0.342 g, 1.55 mmoles) was reacted with coronene (0.464 g, 1.55 mmoles) as described above except no C_6F_6 was used. Removal of solvent gave a free flowing

dark-green powder (0.612 g, 1.55 mmoles if $\text{C}_{24}\text{H}_{12}\text{AsF}_6$).

Anal. Calcd for $\text{C}_{24}\text{H}_{12}\text{AsF}_6$: C, 58.92; H, 2.47%. Found:

C, 57.90; H, 2.67%. The IR spectrum (KBr pellet) is shown

in Figure VI-4. The sample proved to be amorphous to X-rays.

Magnetic susceptibility data are given in Figure VI-5.

Table VI-1 X-ray powder pattern of the green solid product of the reaction of O_2AsF_6 with anthracene (Film No. 1046)

<u>d_{hkl} (Å)</u>	<u>$10^4/d^2$</u>	<u>Relative Intensity</u>
7.95	158	w
6.59	230	mw
6.03	273	w
5.38	345	m
5.04	394	ms
4.83	428	s
4.56	481	s
4.16	577	m
3.52	807	mw
3.43	850	mw
3.03	1087	w

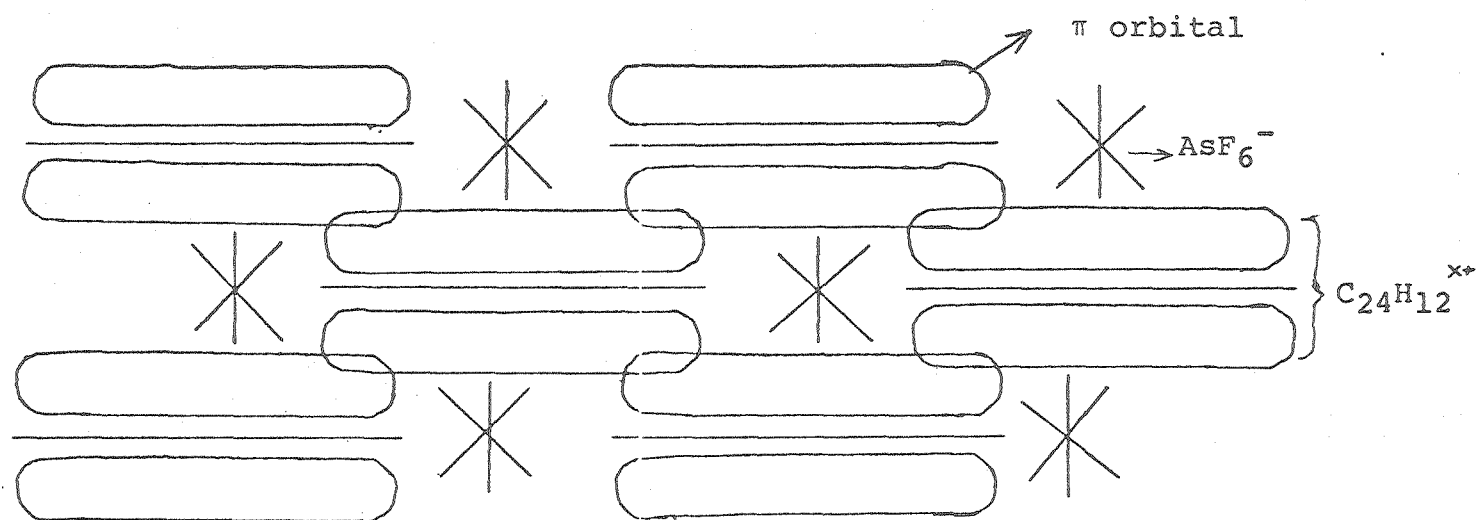


Figure VI-1 Coronene cation-Corononene cation Overlap anticipated for Coronene Salts.

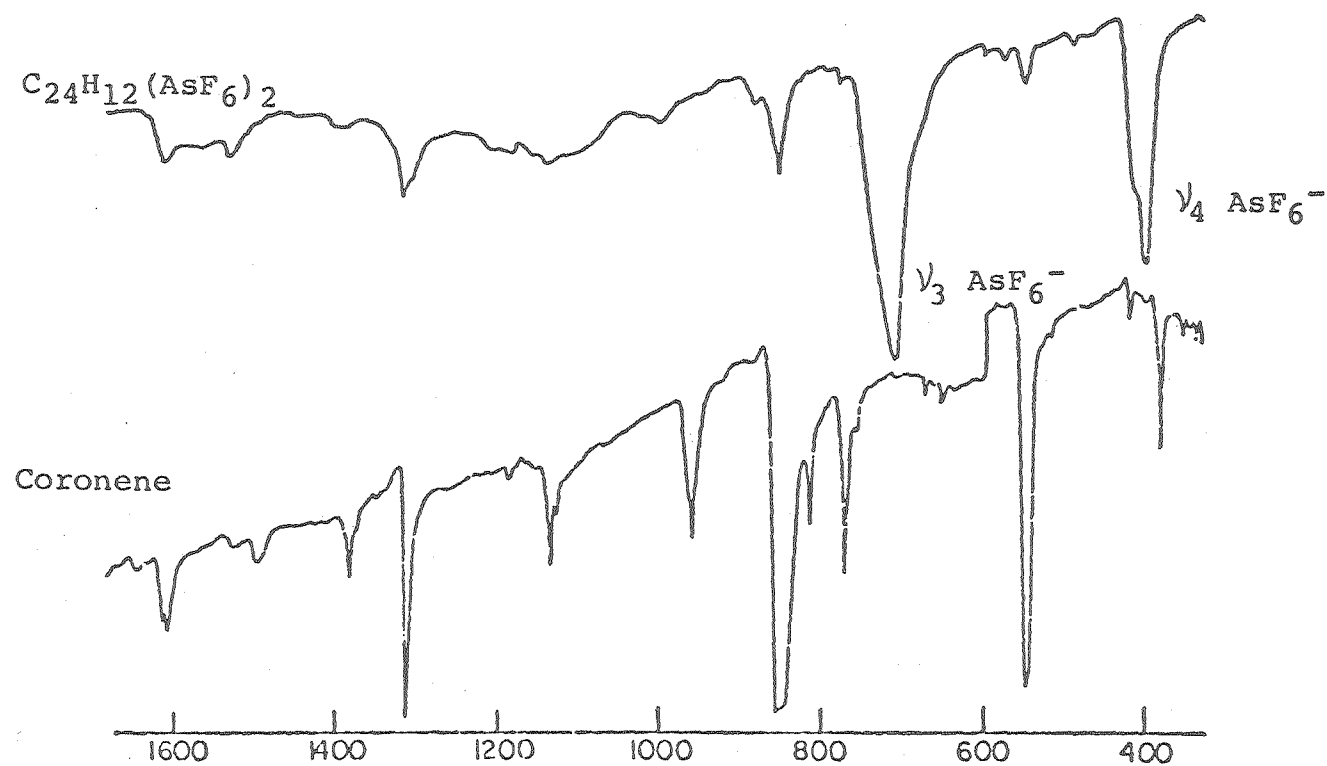


Figure VI-2 IR Spectrum of $C_{24}H_{12}(AsF_6)_2$ and Coronene

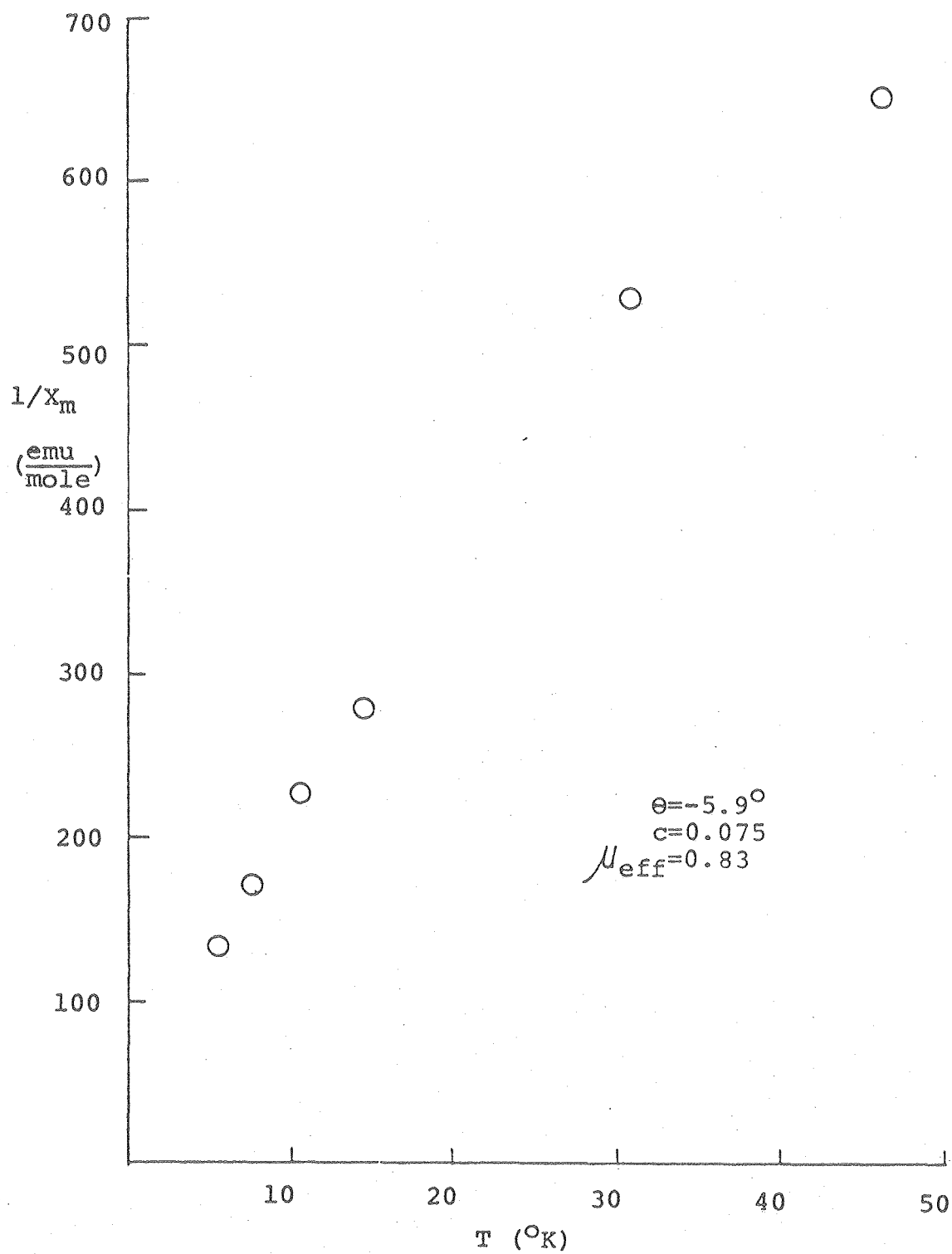


Figure VI-3 Magnetic Susceptibility Data for $\text{C}_{24}\text{H}_{12}(\text{AsF}_6)_2$

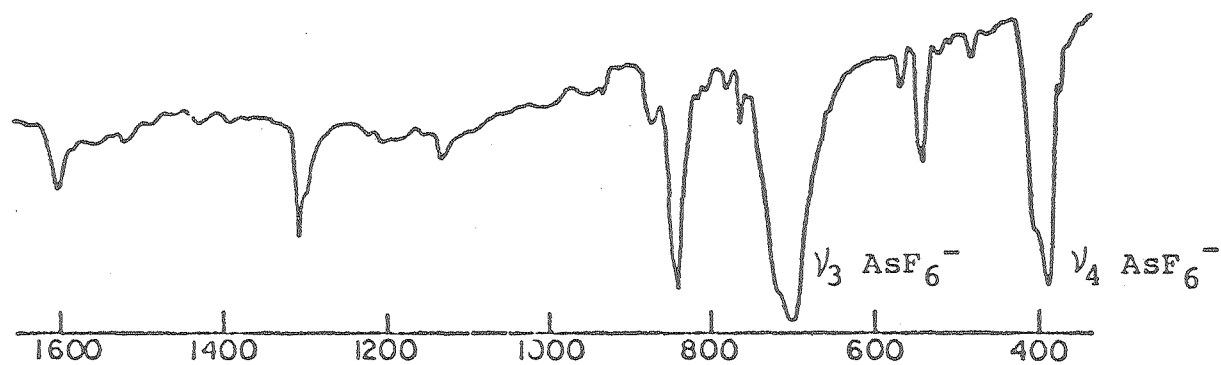


Figure VI-4 IR Spectrum of $C_{24}H_{12}AsF_6$

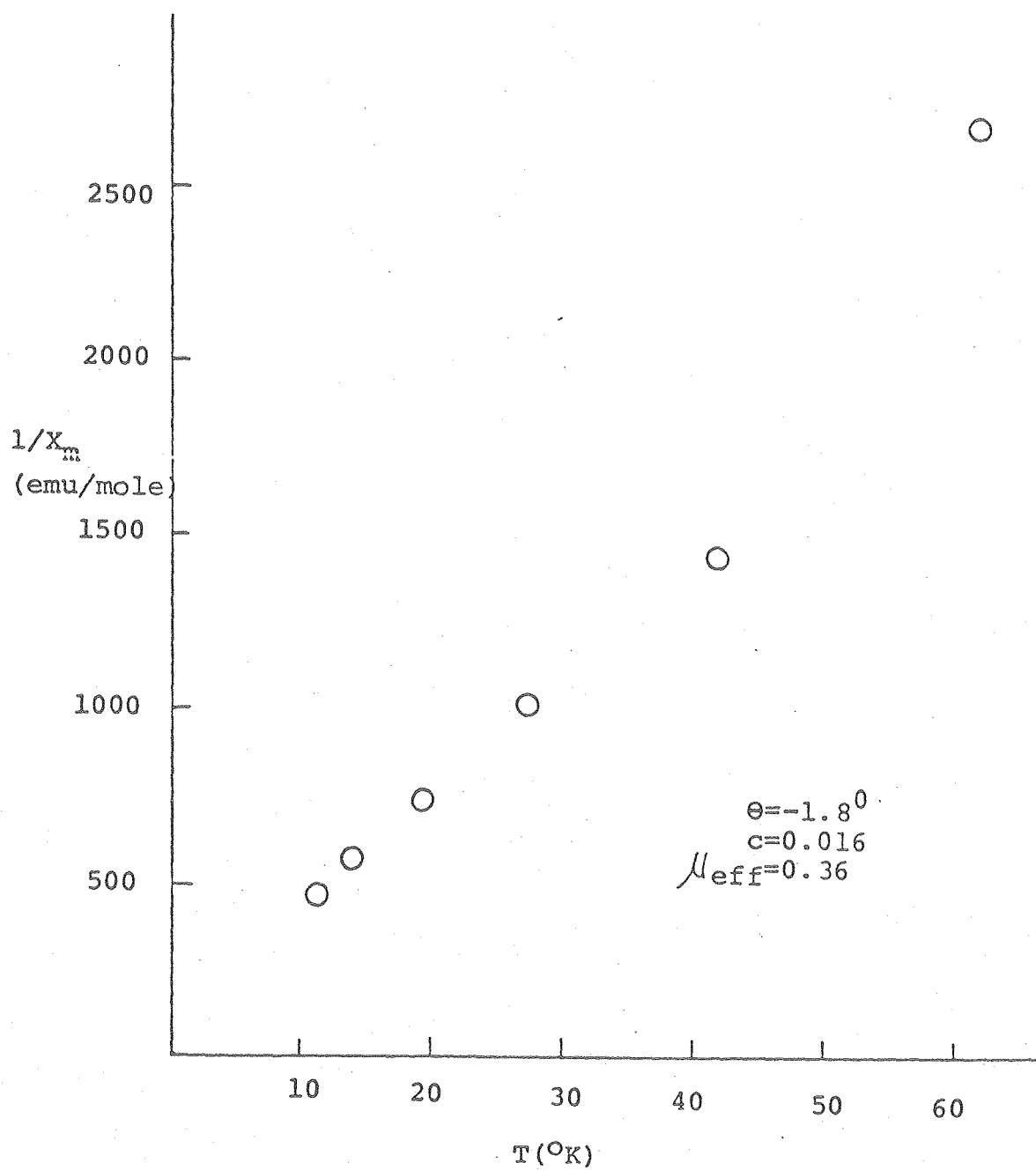


Figure VI-5 Magnetic Susceptibility Data for $\text{C}_{24}\text{H}_{12}\text{AsF}_6$

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